

TECHNICAL METHODS OF  
CHEMICAL ANALYSIS

# TECHNICAL METHODS. OF CHEMICAL ANALYSIS

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## ENGLISH TRANSLATION

FROM THE LATEST GERMAN EDITION, ADAPTED TO ENGLISH  
CONDITIONS OF MANUFACTURE

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## ILLUMINATING GAS AND AMMONIA

By OTTO PFEIFFER, Ph.D., Chemist to the City Gas and Water Works, Magdeburg.  
English translation revised by HAROLD G. COLMAN, D.Sc., Ph.D., formerly Chief  
Chemist to the Corporation Gas Department, Birmingham.

**Introduction.**—The subdivision of the technical methods of chemical analyses pertaining to processes of gas manufacture naturally depends on the sequence of the different portions of gasworks plant.

In coal gas manufacture, retort-house working renders an examination of the fuel required for heating purposes necessary, whether it be in the form of coal or coke, in direct firing, or whether it be burnt indirectly, that is, after conversion into producer gas.

Besides ascertaining the calorific value of the fuel, which is of prime importance, it is necessary for the proper regulation of the retort furnaces to obtain information as to the temperatures in the combustion chambers, retorts, and flues. These temperatures afford information, on the one hand, concerning the uniformity of heat distribution and also its intensity and constancy, and, on the other hand, when taken in conjunction with the analysis of the waste gases, concerning the loss of heat resulting from the escaping main flue gases. The regulation of dampers, and the measurement of draught in the various flues and other parts of the retort setting, are also subjects for consideration.

As raw material, the *Gas Coal* subjected to destructive distillation is naturally of the greatest importance. Though many useful data for judging its gas-making value are doubtless afforded by complete analysis, it is nevertheless necessary to have recourse to practical tests in order to arrive at reliable conclusions. The examination of benzol and of carburine for carburetting at ordinary temperatures, and of gas oils for enriching water gas at high temperatures, is also of value.

The *Composition of the Gas* is a subject of investigation from various points of view. In the first place, gas analysis is very helpful in regulating the working of the retort setting, in that the producer gases, as well as their products of combustion, require to be studied on the lines suggested. The manufactured gases to be considered are:—Coal gas (crude gas and town gas), wood and peat gas, oil gas, water



gas (blue gas and carburetted water gas), and mixed gas (Dowson gas, etc.).

The *Purified Gases of Manufacture* may be submitted to one general method of analysis. Certain impurities which have to be estimated in crude gas by special means, are determined by the same methods also in town gas.

In addition to the analysis of gas, the calorific value, specific gravity, and illuminating power have to be ascertained.

As a by-product of gas manufacture, *Spent Oxide* is of considerable value as a saleable article, since it contains not only sulphur, but also compounds of cyanogen and ammonia, and, therefore, the percentages of these constituents have often to be ascertained. Periodical analyses of its composition are also of value for the control of the purifying plant, as it enables the action of the material in the purifier boxes to be more closely watched. New oxide should be examined for its content of active ferric hydroxide, its absorptive power for sulphuretted hydrogen, and its density.

As regards *Gas Liquor*, the specific gravity and ammonia content are the more important data to be ascertained. In rare instances an analysis of the acid constituents may be desirable. The analysis of gas liquor bears on the working up of this by-product for ammonia and ammonia salts, the production of which is often undertaken in the larger gas works. In the manufacture of ammonia by heating the liquor with lime, it is necessary to analyse the quicklime used, to ascertain how much must be added to the liquor. The finished ammonia liquor must be tested for strength as well as for purity, and this applies also to salts of ammonia.

The analysis of *Coke* is carried out by the methods applicable to other fuels.

The examination of *Tar* is dealt with in a separate section (this Vol., pp. 750 to 844).

This list by no means embraces all the chemical tests appertaining to gas manufacture. It is intended to serve merely as a guide to the routine of work that is required.

### I.—WORKING OF RETORT SETTINGS

In modern coal gas manufacture, two methods of heating the retort settings are in use, namely: (1) Direct fired settings; (2) Generator settings, in which the solid fuel is first converted into generator or producer gas, the latter being burnt in the setting by the admission of a secondary supply of air. In most cases the gas-fired settings are also provided with a regenerator, in which a large proportion of the heat of the waste gases is recovered by transferring it to the secondary air

on its way into the setting. In the great majority of cases a separate generator is provided for each bed of retorts, but in some works the generator is made large enough to supply sufficient gas for the heating of from two to four beds, and in a few large works outside producers are employed, of sufficient size for heating the whole of the beds in the retort house.

The fuel employed is almost invariably the coke drawn from the retorts. The methods of carrying out the elementary analysis of coke, and for the determination of its calorific power, are described under "Fuel" in Vol. I., p. 241.

The direct fired settings, in which the coke is burnt on the furnace hearth with a sufficient supply of air to effect complete combustion, are still employed in many of the smaller and some of the larger works, but are being steadily replaced by some form of generator setting, on account of the great economy of fuel effected by the latter, and of the higher and more regular temperatures which can be obtained. With the direct fired settings the whole of the heat due to the combination of the oxygen of the air with the carbon and hydrogen of the fuel takes place in the furnace itself, and the heating of the setting is effected solely by the sensible heat of the products of combustion; in order to heat the setting throughout, it is necessary that these should still have a high temperature at the extreme end, and they, therefore, leave the setting and pass away to the chimney still very hot, and the heat remaining in them is wasted. Hence, the amount of fuel used with a direct fired setting amounts to from 25 to 30 parts of coke per 100 parts of coal carbonised. With such settings very little assistance in working can be obtained from analyses of the waste gases, good results being mainly dependent upon proper attention being paid to the furnace by the fireman.

In the generator settings, the general object in view is the production in the generator of a sufficient quantity of generator or producer gas for the proper heating of the retorts by the admission of limited quantities of air (primary air) and steam below the fire bars in the generator, the producer gas being then completely burnt within the setting by the admission of a secondary supply of air, the amount of which is regulated as nearly as practicable to the quantity just necessary to effect the complete combustion of the furnace gas. It is also important that the whole of the furnace gas and secondary air should not combine immediately at the point at which the two streams mix, but rather that these should flow side by side for some distance, and slowly undergo combustion, so that the heat of combination may be evolved gradually as the gases pass along the setting, thus heating the latter as nearly as possible to a uniform temperature. Combustion should, however, be complete before the gases reach the end of their

course within the setting, and pass to the chimney or enter the regenerator flues. Too rapid mixing of the furnace gas and secondary air at an early stage results in the production of too high temperatures at this point and too low temperatures farther on, which is not only detrimental to good carbonisation, but may also cause very serious damage to the brickwork at the first point.

#### A. THE ANALYSIS OF FURNACE AND WASTE GASES

The experienced observer is able to judge with a considerable degree of accuracy how far the heating of the setting is proceeding in a satisfactory manner, by inspection of the retort temperatures, and those within the setting and flues, as estimated by the eye through the sight holes provided, and to adjust the dampers and the primary and secondary air slides so as to give a proper production of furnace gas, and to avoid any large excess or deficiency of secondary air. The exact regulation can, however, only be obtained by combining such observation with the information obtained from the analysis of the furnace and waste gases; such analyses are especially of value in obtaining a low fuel consumption and in the detection of leakage of air into the flues owing to the development of cracks or faulty joints.

**1. Furnace Gases.**—The furnace gas, formed by the admission of limited quantities of air (primary air) and steam below the fire bars of the generator, consists of a mixture of small quantities of carbon dioxide, with larger amounts of carbon monoxide and hydrogen, together with all the nitrogen of the primary air. In addition, small quantities of methane (0.5 to 2.0 per cent.) are usually present, but it is, as a rule, hardly necessary to ascertain the quantity of this constituent for the purpose of controlling the heating of the setting. The amount of hydrogen varies considerably, according to the quantity of steam evaporated from the water contained in the ash pan and from that dropped on to the fire bars to keep them cool and prevent their burning through. In some cases steam under pressure is also blown in beneath the fire bars, and a larger percentage of hydrogen and a lower percentage of nitrogen is then present in the gas.

For the collection of the samples, Pfeiffer employs a  $\frac{1}{2}$ -inch iron pipe about a yard in length, in which is placed a porcelain tube (No. 2008, Royal Berlin Porcelain Factory), the latter passing through a cork at one end of the iron tube. The open end of the latter is placed in the furnace, and the porcelain tube then pushed through the cork until the end projects into the fuel, the gas sample being then aspirated through the tube either into the gas analysis burette direct or into sample tubes or bottles.

The methods of analysis employed are described in the section on "Technical Gas Analysis" (Vol. I., pp. 189 *et seq.*), the Hempel, Orsat, or Bunte apparatus being mostly employed. Pfeiffer prefers to estimate the carbon monoxide by combustion and not by absorption with cuprous chloride, the gas after removal of carbon dioxide being mixed with a sufficient excess of air and passed over heated palladium asbestos; the contraction of volume multiplied by two-thirds gives the volume of hydrogen present, that of carbon monoxide being subsequently ascertained by absorption of the carbon dioxide produced, with potassium hydroxide.

The calculation of the calorific value of the furnace gas may be made according to the general rules for the calculation of this value from the analytical results (p. 694). For ordinary purposes it is sufficient to multiply the combined percentages of hydrogen and carbon monoxide by 3.45 to obtain the gross value in British Thermal Units per cubic foot of the dry gas at 32° F. and 30 in. pressure, or by 30.6 to obtain the gross value in calories per cubic metre at 0° C. and 760 mm. pressure.

Thus, the gross calorific power of a furnace gas containing 24.5 per cent. of CO and 17.2 per cent. of H<sub>2</sub> is approximately:—

$$\begin{aligned} (24.5 + 17.2) \times 3.45 &= 137.6 \text{ B.Th.U. per cubic foot} \\ \text{or} \quad (24.5 + 17.2) \times 30.6 &= 1276 \text{ Cal. per cubic metre.} \end{aligned}$$

\* The percentage of carbon dioxide in the furnace gas should not exceed about 6 per cent. in good working. Should a high percentage be found, together with a high percentage of nitrogen, it usually indicates leakage of air into the generator above the fuel bed, owing either to insufficient tightness of the generator-charging door, or to leakages in the brickwork.

**2. Waste Gases.**—The collection and analysis of the waste gases is carried out in a similar manner to that of the furnace gases, and for practical purposes it is only necessary to determine the amounts of carbon dioxide, oxygen, and carbon monoxide. If carbon monoxide be present, small quantities of hydrogen are also contained in the gas, but the amount is rarely sufficient to make its estimation worth while. Unless the percentage of oxygen found is very small, it is unnecessary to test for either carbon monoxide or hydrogen.

From the analysis of such samples the secondary air slides can be regulated to supply just sufficient oxygen to effect the complete combustion of the furnace gas, and in addition, by the analysis of samples taken simultaneously at different points in the regenerator, short-circuiting of the air from the secondary air flues into the waste gas passages owing to cracks or faulty joints, may be detected. This is

exemplified in the following series of analyses of samples taken from a bed of retorts which had been at work for a long time:—

	CO <sub>2</sub> .	CO.	H <sub>2</sub> .	O <sub>2</sub> .
	Per cent.	Per cent.	Per cent.	Per cent.
1. Around retorts (a) . . .	18.5	2.7	1.4	...
2. " " (b) . . .	19.4	0.6	0.3	...
3. Entrance to 1st flue . . .	19.3	...	...	0.3
4. " " 2nd " " . . .	18.4	...	...	0.6
5. " " 3rd " " . . .	14.0	...	...	6.4
6. " " 4th " " . . .	7.2	...	...	13.0
7. Chimney gases . . .	7.2	...	...	13.2

In this instance the combustion was completed with a slight excess of oxygen at the beginning of the regenerator, but in passing through the successive flues a very large amount of air leaked into the waste gases, chiefly between the fourth and sixth points at which the samples were taken.

When it is only desired to determine the "neutral zone" of combustion, *i.e.*, the point at which free oxygen first appears in the mixed gases, a quantitative examination is unnecessary, as this may be quickly ascertained by a simple apparatus devised by Pfeiffer.<sup>1</sup> This consists of a calcium chloride tube about 30 c.c. in length, in which are placed a few thin sticks of yellow phosphorus, about 15 c.c. long (Fig. 89). The lower end is closed with a cork fitted with a doubly bent glass tube, and the whole is placed in a jar containing sufficient water to cover the phosphorus and prevent its oxidation by the air.

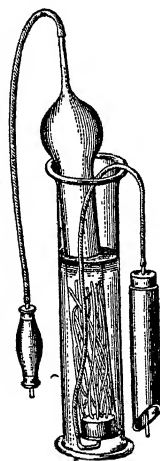


FIG. 89.

To use the apparatus, the tube containing the phosphorus is lifted out of the jar and the water allowed to drain out; the bent glass tube is then connected to the porcelain tube through which the sample is drawn from the flues, the upper end to a rubber aspirator, and the tube then replaced in the water to protect it from the heat radiated from the setting. The temperature of the water must not fall below 15°, as phosphorus does not combine with oxygen below this temperature. The flues are then tested in order from top to bottom, and as soon as oxygen is present in appreciable quantity thick white fumes of phosphorus oxides are formed. A slight mist is formed at each suction stroke of the aspirator, due to the deposition of moisture owing to the cooling of the gas by expansion, but this is quite distinct in appearance from the phosphorus fumes and cannot be mistaken for them.

<sup>1</sup> *J. Gasbeleucht.*, 1898, 41, 605.

In taking the samples of the furnace and waste gases, great care is necessary to ensure that they are collected at such times as the setting is working under normal conditions. If, for example, the samples are taken at a period shortly before the furnace is due for clinkering, an excess of oxygen will most probably be found in the waste gases, as, owing to the accumulation of clinker, the gas production is then below the average, and *vice versa*, just after clinkering, an excess of carbon monoxide is usually found in the waste gases, owing to the gas production being above the normal. Any adjustment of the secondary air slides based on such analyses would in either case result in a wrong proportion of secondary air for the conditions prevailing over much the greatest period of time. Samples should, therefore, not be taken for control purposes either too soon before or after clinkering, and further, when excess of oxygen is found in the waste gases, it is always advisable to make certain that this excess is not a temporary one caused by negligent handling of the furnace, such as insufficient care in keeping the clinker from collecting on the fire bars, which then obstructs the passage of the primary air and steam into the furnace, and lowers the gas production. For the purpose of controlling the secondary air supply, the samples of waste gases must be taken before the regenerator, as samples taken after the latter are apt to contain additional quantities of air owing to the above-mentioned short-circuiting in the regenerator; in such a case regulation of the secondary air slides to give a slight excess only of oxygen at that point, would result in a deficiency of air in the setting itself.

When any changes are made in the dampers or air slides, an interval should be allowed to elapse before any further tests are made, so as to give time for normal working to be attained under the altered conditions. This is especially the case with regard to the observation or determination of temperatures, which, owing to the large mass of brickwork in the setting, often take some hours to show any appreciable change.

Further, while the analyses are of very great value when taken in combination with accurate observation of the working of the setting in other respects, it is to be remembered that the blind regulation of the air slides and dampers based on such analyses alone may be productive of much more harm than good. Thus, whilst analysis gives the composition of the furnace gas, it affords no indication of the quantity being produced, and if the quantity be either too small or too large, it is quite possible to adjust the secondary air slides to give a good analysis of the waste gas; but in the former case the retorts would not be properly heated, and in the latter great waste of fuel would occur. Again, although the proper amount of furnace gas may be produced, and a good analysis of the waste gas obtained, the latter

only shows that combustion is completed within the setting without undue excess of air, but gives no indication as to whether the combustion is proceeding in the desired manner, namely, gradually throughout the setting, or whether, owing to rapid mixing of the furnace gas and secondary air at an early stage, too great evolution of heat takes place at that point, resulting in irregular heating, and the development of "cutting" heats, which materially damage the brickwork. The gradual combination of the gas depends less on the composition and proportions of the gases than on the design of the setting, especially the manner in which the furnace gases and secondary air impinge on each other at the point of mixing, and on the extent to which the gas streams are baffled in their onward passage.

### B. TEMPERATURE MEASUREMENT

For the measurement of temperatures in the retort setting flues, and in the retorts themselves, many different forms of pyrometer are now available. These have already been described in Vol. I. (pp. 174-185). The temperatures to be measured vary from about 1000 to 1400° C. (1830° to 2550° F.) in the retort setting, and from 300 to 600° C. (570° to 1100° F.) at the chimney stack.

In taking temperatures within the setting and flues it is to be borne in mind that the different types of pyrometer will give different results, according as they measure the temperature of the glowing brickwork or the temperature of the hot gases at that point, for, as the heating of the brickwork is affected by the heat of the gases, the temperature of the latter is always appreciably higher. Hence, the optical instruments, such as the Wanner and Féry pyrometers, which record the temperature of the brickwork, give a somewhat lower result than the thermo-electric, electric resistance, or calorimetric pyrometers, which record the temperature of the gases. In the interior of the retorts themselves, provided there is no draught of air through them, the temperature of the walls and of the gases are in equilibrium, and the different types of pyrometers should give the same result.

For the general determination of temperatures in the setting, where these are always above a red heat, the optical pyrometers are the most convenient, as no part of the instrument has to be placed within the setting. A simpler form of the Féry instrument has been recently introduced,<sup>1</sup> in which the thermopile and galvanometer are replaced by a delicate metallic thermometer, which is graduated in such a manner that the furnace temperatures are read directly. This apparatus is especially useful for places similar in character to the retort house, and whilst the results are probably not quite so exact as those obtained

<sup>1</sup> Supplied by the Cambridge Scientific Instrument Co.,

with the more expensive instrument, they are of quite sufficient accuracy for all ordinary purposes.

For the flues, where lower temperatures prevail, the Le Chatelier pyrometer (with the modification described by Pfeiffer, Vol. I., p. 183) gives excellent results. For the temperature of the retorts, the Féry pyrometer is also the most convenient instrument, as it enables the temperatures of a large number of retorts to be taken very quickly. The Le Chatelier, Callendar, Wannier, and Siemens water pyrometer, and the Seger cones are, however, frequently employed.

### C. DETERMINATION OF PRESSURES

The measurement of pressure in the different parts of the setting is also of great assistance in regulating the working. Under normal conditions the draught steadily increases from the top of the retort setting to the chimney, and any sudden alteration, if found, indicates either a block in the flues between the two points where the alteration in pressure occurs, or the leakage of large quantities of air from the secondary air into the waste-gas flues. Which of the two alternatives has actually occurred is determined by analysis of the gas at the same points as those at which the pressures are taken, as if the latter is the cause, a large increase will also be shown in the percentage of oxygen present.

The various instruments for pressure measurement are described in Vol. I., pp. 165 to 172.

### D. FUEL CONSUMPTION OF RETORT SETTINGS

In ascertaining the exact fuel consumption, a figure often required for statistical purposes as well as in the trial of new settings, the total make of coke must also be determined. The test should extend over at least twenty-four hours. The coal used for charging the centre retorts, from which the fires are usually fed, is carefully weighed, the coke from two or three of these retorts discharged into a tared wagon, which is then closed to exclude air, and weighed. It is then only necessary to count the number of retort charges used for the fires, taking care also that the furnace is equally full both at the beginning and end of the test.

*Example.*—Weight of charge: 336 lbs. of gas coal; total weight carbonised in twenty-four hours with a bed of 9 retorts, duration of charge being six hours:  $9 \times 24 \times 336 \div 6 = 12096$  lbs. Yield of coke from 336 lbs. of coal: 231 lbs. = 68.8 per cent.; fuel used under the retorts: 6 retorts of coke. Thus, Fuel Consumption  $= 336 \times 0.688 \times 6 = 1390$  lbs. coke = 11.5 per cent.



E. LOSS OF HEAT IN WASTE GAS (Bunte).<sup>1</sup>

For every fuel, the percentage of carbon dioxide in the products of combustion corresponds to a theoretical temperature of combustion which will be highest when just sufficient air is present to effect complete combustion, under which conditions the percentage of carbon dioxide in the waste gases is also at its maximum. This temperature is diminished by excess of air, which at the same time lowers the content of carbon dioxide of the waste gases, so that, in proportion to the latter, there is a corresponding definite initial temperature  $T$ . If the temperature,  $t$ , of the waste gases be known, then the loss of heat through the stack =  $\frac{t}{T} \times 100$ . In the following table the initial temperatures have been calculated for carbon, but they can be applied also to coke firing. The figures are inaccurate, however, when the waste gas temperature exceeds  $400^\circ$ , and above this limit the calculated values are only useful for comparison.

CO <sub>2</sub> Content. Per cent.	Initial Temperature. Degrees C.	Difference for 0.1 per cent. CO <sub>2</sub> .	CO <sub>2</sub> Content. Per cent.	Initial Temperature. Degrees C.	Difference for 0.1 per cent. CO <sub>2</sub> .
1	141	14	11	1490	13
2	280	14	12	1620	13
3	419	14	13	1750	13
4	557	14	14	1880	13
5	694	14	15	2005	12
6	830	14	16	2130	12
7	967	13	17	2255	12
8	1096	13	18	2375	12
9	1229	13	19	2500	12
10	1360	13	20	2625	12

For example, if the average amount of CO<sub>2</sub> in the chimney gases has been found to be 9.8 per cent. and the temperature  $385^\circ$ , the loss of heat is  $= \frac{385 \times 100}{1334} = 28.9$  per cent.<sup>2</sup>

## II.—GAS-MAKING MATERIALS

## A. GAS COAL

1. **Chemical Valuation.**—A coal suitable for gas-making purposes should, in addition to yielding a large volume of gas of suitable illuminating and calorific power, yield a coke of saleable quality. Such coke is only produced by those bituminous coals which become plastic

<sup>1</sup> Cf. *J. Gasbeleucht.*, 1878, 21, 62; and Muspratt's *Handbuch der technischen Chemie*, 4th ed., vol. iv., p. 299.

<sup>2</sup> Cf. also Vol. I., p. 237.

and semi-fused on heating, thus yielding, on further carbonisation, a coherent coke totally different in shape and structure from that of the original coal. These coals are classed together under the general name of "bituminous caking coals." Non-caking coals are only used in exceptional cases, such as the employment of cannel coal where gas of very high illuminating power is desired, or where, owing to local conditions, such coals can be obtained at a price sufficiently below that of the caking coals to compensate for the lessened value of the coke produced.

*Elementary or Ultimate Analysis.*—The methods of elementary analysis are described in the section on "Fuel" (Vol. I, pp. 242 *et seq.*).

It is very generally held, even by experts, that it is not possible to derive from the elementary analysis of coal any useful information as to its suitability for gas-making purposes, since the analyses of coals, even from one and the same seam, give figures varying between wide limits; also it is regarded as quite impossible to arrive at a representative sample by taking small quantities at a time. These objections largely disappear if, in the coal analyses, the figures for moisture and ash are eliminated (which certainly vary in different parts of the same seam), and only the remaining figures are taken into account—*i.e.*, the pure coal substance, according to its percentage content of carbon, hydrogen, and oxygen (+N+S). Analytical results referred in this way to a common basis of comparison show, as a matter of fact, very close concordance in the case of coals of the same origin, so that it is quite possible to judge of their general qualities as gas coals from the chemical composition. According to Bunte,<sup>1</sup> who was the first to lay down these relations, the most important German gas coals have the following average composition:—

	Per 100 parts of Coal substance.		
	Carbon.	Hydrogen.	Oxygen (+N+S).
Westphalian gas coal. .	85·39	5·44	9·17
Silesian " . .	84·80	5·30	9·90
Saarbrück " . .	84·45	5·43	10·12
Bohemian " . .	82·65	5·88	11·47
Saxon " . .	82·38	5·74	11·88

As a result of numerous gas-making tests on the coal-testing plant at La Villette Gas Works, Paris, Sainte-Claire Deville classifies all the coals suitable for gas-making into five groups, according to their oxygen content, the gradual diminution of which is intimately connected with the age of the coal. In the following tabular statement the numerous relations between the coals, thus classified according to their composi-

<sup>1</sup> *J. Gasbeleucht.*, 1888, 31, 895.

tion, and the make and quality of the gas produced by distillation, are given, the figures being the average values of the tests made:—

	Type I.	Type II.	Type III.	Type IV.	Type V.
100 parts of coal- substance contain { Oxygen . . . . .	5.56	8.68	7.71	10.10	11.70
{ Hydrogen . . . . .	5.06	3.37	5.49	5.53	5.61
{ Carbon . . . . .	88.38	86.97	85.89	84.37	81.66
{ Nitrogen (approx.) . . . . .	1.00	1.00	1.00	1.00	1.00
Moisture content of air-dried raw coal . . . . .	2.17	2.70	3.31	4.35	6.17
Total weight of distillation products . . . . .	26.82	31.59	33.80	37.34	39.27
„ „ coke . . . . .	73.18	68.41	66.20	62.66	60.73
Gas, per cent. by weight on coal-substance . . . . .	13.70	15.08	15.81	16.95	17.00
Tar . . . . .	3.90	4.65	5.08	5.48	5.59
Virgin gas liquor . . . . .	4.58	5.22	6.80	8.62	9.86
COMPOSITION OF THE GAS IN PER CENT. BY VOLUME.					
Carbon dioxide . . . . .	1.47	1.58	1.72	2.70	3.13
Carbon monoxide . . . . .	6.68	7.19	8.21	9.85	11.33
Hydrogen . . . . .	54.21	52.79	50.10	45.45	45.26
Methane and Nitrogen . . . . .	34.37	31.43	35.03	36.42	37.11
Heavy hydrocarbons . . . . .	3.27	4.01	4.94	5.58	5.51
Specific gravity of the gas . . . . .	0.352	0.376	0.399	0.441	0.482
Gas consumption for equal candle power . . . . .	132.1	111.7	103.8	102.1	101.8

According to the above results, coals of Type III. (7.5 to 9 per cent. O) are the best gas coals, since they yield a large make of rich gas as well as coke of good quality. Coals of Types I. and II. produce a large quantity of coke, but a poor yield of gas, whilst Types IV. and V. yield gas of high illuminating power, but, on the other hand, the coke is poor in quality and small in quantity. The production figures, however, ought not to be generalised; they can only serve for comparison on the basis that the conditions of manufacture were always the same.

*Calorific Value of Coal.*—The methods for the determination of calorific power are described in the section on Fuel (Vol. I., p. 250), where the means of determination by direct experiment and by calculation from the ultimate analysis are given.

*Proximate Analysis of Coal.*—For most gasworks purposes, a complete elementary analysis of coal is rarely required, the "proximate" analysis being usually sufficient. This consists in the determination of the percentage of ash, moisture, volatile matter other than free moisture, and residual coke. In addition, the percentage of sulphur, both in coal and coke, is also frequently required, and is ascertained by the methods already given (Vol. I., p. 245).

The quantity of volatile matter, *i.e.*, the loss of weight (excluding free moisture), found when the coal is strongly ignited in absence of air (which conversely also gives the weight of residual coke) is not, like the elementary composition of the coal, an absolute quantity, but varies considerably according to the manner in which the heating is carried out, and the coke yields obtained in the laboratory test frequently also differ materially from those obtained with the same coal in gas retorts and coke ovens. In order, therefore, to obtain comparative values of coals in this respect, it is essential that standard conditions should be adhered to in carrying out the test.

Numerous methods of procedure have been proposed, the three most frequently employed being the original method suggested by Muck,<sup>1</sup> the Bochum method,<sup>2</sup> and the American method.<sup>3</sup>

In Muck's method, 1 g. of powdered coal is heated in a medium-sized crucible not less than 3 cm. in height, having a close-fitting lid, the crucible being supported so that the bottom is about 3 cm. above the top of a burner giving a flame not less than 18 cm. high. The heating is continued as long as any perceptible flame issues from between the crucible and lid.

In the Bochum method, a crucible of from 22 to 35 mm. in height is used, closed with a lid having a hole in the centre 2 mm. in diameter. The height of the bottom of the crucible above the burner is increased from 3 cm. to 6 cm., so that the former is in the oxidising flame. A flame fully 18 cm. long is employed for heating, which is continued until gas no longer burns at the hole in the crucible lid. This method gives a higher coke yield than that of Muck, and the results are more nearly in agreement with large scale working.

The American method, recommended by the American Chemical Society's Committee on Coal Analysis, is as follows:—One gram of undried, powdered coal is placed in a platinum crucible of 20 to 30 g. weight having a closely fitting lid which is supported in such a manner that the crucible bottom is from 6 to 8 cm. above the top of the burner. An ordinary Bunsen burner is employed, giving a flame at least 20 cm. long when burning free, and the heating is continued for seven minutes. The determination should be carried out in a place free from draughts. The upper surface of the crucible lid should be free from carbon after the estimation, whilst the under surface should remain covered with a black film.

During the past few years a very exhaustive investigation of the subject has been carried out in the Swiss National Fuel Testing Station at Zürich by Constam, who with his co-workers has carried out tests by the various methods with a very large number of coals of widely different origin. As a result, he considers that the American method

<sup>1</sup> *Chemie der Steinkohlen*, 2nd edition, p. 10.

<sup>2</sup> *Z. angew. Chem.*, 1904, 17, 738.

<sup>3</sup> *J. Amer. Chem. Soc.*, 1899, 21, 1122.

should be recommended for general adoption, for the following among other reasons:—(1) It gives the best agreement between parallel estimations with the same sample of coal; (2) the results are the least influenced by variation in the size of crucible and flame temperature; (3) it gives results more nearly in accordance with those obtained in practice in gasworks and coke ovens than any other method, and the composition of the coke is less affected by the nature of the original coal than is the case with other methods.

In all cases the quantity of free moisture, found by separate experiment, must be deducted from the loss of weight found, in order to ascertain the weight of volatile matter. For the purpose of making comparisons between the volatile matter present in different coals, the percentage of "volatile matter" should be calculated on the actual weight of *coal substance* in the coal—*i.e.*, the weight of coal after deduction of the ascertained percentages of moisture and ash.

**2. Direct Valuation of Coal by Distillation.**—The full estimation of the practical yield of a coal sample, both in regard to quantity and quality of gas, can only be ascertained by actual tests with the gasworks plant in normal working, as the conditions of small scale testing inevitably differ too much from those prevailing in everyday practice. In some works a special experimental plant is provided in which arrangements are made for the supply of gas from one or more beds of retorts, to be passed when required through a separate plant consisting of condensers, exhauster, scrubber, purifier, meter, and gasholder, suitably arranged for testing purposes.

Small scale-testing plants, modelled to represent large scale working as nearly as possible, almost always give higher results from any coal than can be obtained in actual working. Nevertheless the results obtained with such plant are often of great value, as although the absolute figures given may attribute too high a value, they enable a fair estimate to be obtained of the *relative* value of coals for gas-making purposes; also, they provide a means of checking the value of coals supplied to ascertain if these are up to sample. The size of such test plants varies considerably, the smallest size being for 2.24 lbs., or  $\frac{1}{1000}$  of a ton, whilst others receive a charge of from 22.4 to 112 lbs., and, as a rule, the smaller the apparatus the higher are the results obtained from the same sample. It is, therefore, generally undesirable to make any comparison of the tests made with one plant against those made in another place with a different plant; the comparison should always be confined to tests made on one and the same apparatus. Further, in using such plants, very great care is required in sampling, to ensure that the coal put into the retorts fairly represents the bulk to be tested, and the smaller the retort used the greater is the care necessary in this respect.

With such an apparatus, the yield of gas, its illuminating and calorific power and specific gravity, can be determined with a considerable degree of accuracy, as well as the yield of dry coke. Measurements of the yield of tar and ammonia are, however, not made satisfactorily. The methods of testing illuminating power, calorific power, and specific gravity are described later, but it should be mentioned here, that where it is a matter of determining the comparative value of coals, it is essential that the illuminating power shall be ascertained by a method which gives as nearly as possible the true comparative value of gases of widely differing illuminating power, which is very far from the case with many of the statutory methods of determining the latter. For ordinary coals, the most suitable method is to employ the Metropolitan No. 2 Argand burner, burning the gas at the rate of 5 cb. ft. per hour with the air damper adjusted so that the flame is just short of the smoking point; or, if the London No. 1 Argand be employed, the gas should be consumed at such a rate as to give a chimney full of flame without smoking, and the illuminating power for 5 cb. ft. calculated from the observed rate of consumption. These methods give results which are comparable, so far as tests made with the same burner are concerned, but as the actual illuminating power given with the same gas by the No. 2 burner is higher than that given by the No. 1 burner under the conditions named, no comparison must be made between tests made with the different burners.

The gas yield must be reduced to standard temperature and pressure, which, however, in the British gas industry is not the usual normal of dry gas at  $0^{\circ}\text{C}$ . and 760 mm., but of moist gas at a temperature of  $60^{\circ}\text{F}$ . and 30 in. pressure. Apart from the use of British units, the temperature actually taken is different, the reason being that a Gas Undertaking sells its commodity by volume and not by weight, and the standard temperature for measuring the volume has, therefore, been fixed by statute as  $60^{\circ}\text{F}$ ., this being assumed to be the average temperature at which it is measured in the consumers' meters. Hence the term "normal temperature and pressure" for gas works purposes differs from that employed for scientific purposes. In the subsequent pages, wherever it appears advisable, figures are given, both corrected to  $0^{\circ}\text{C}$ . and 760 mm. (dry gas), and to  $60^{\circ}\text{F}$ . and 30 in. pressure (moist gas), the latter figures being practically identical with those for  $15^{\circ}\text{C}$ . and 760 mm., which is frequently also employed as standard in the gas industry on the Continent.

To obtain a figure representing the comparative value of a coal sample, so far as its combined results for yield and illuminating power are concerned, two methods are in use. In one, the comparative value is obtained by simply multiplying together the yield of gas per ton of coal and the illuminating power, the product being known as the

"multiple" of the coal. In the other, the results are expressed in "sperm value"—*i.e.*, the number of pounds of sperm (as used in the manufacture of the statutory standard candle) equivalent in light-giving power to 1 ton of coal. As each standard candle burns at the rate of 120 grains, or  $\frac{120}{7000}$  lb. per hour, and the illuminating power of the gas is taken for a consumption of 5 cb. ft. per hour, the sperm value is obtained by the formula—

$$\text{Sperm value} = \frac{\text{Yield in cb. ft. per ton} \times \text{illuminating power} \times 120}{5 \times 7000}$$

Or, working out the constants :—

$$\text{Sperm value} = \text{Yield per ton} \times \text{illuminating power (multiple)} \times 0.00343.$$

For calorific power, the multiple of yield per ton by the calorific power in B.Th.U. per cubic foot is usually employed, this calorific multiple, therefore, representing the total yield of B.Th.U. per ton of coal in the form of combustible gas.

#### B. ANALYSIS OF OILS EMPLOYED IN THE MANUFACTURE OF CARBURETTED WATER GAS

The oil employed in the manufacture of carburetted water gas in Great Britain and Ireland is always derived from petroleum or shale oil, the fraction commonly used, on account of its relatively low price, being that intermediate between the burning oils on the one hand and the lubricating oils on the other.

The various samples of oil differ considerably in the chemical nature of their constituents, according to the source from which they are derived; their exact value for gas-making purposes is best ascertained by tests made on a working scale, as only in this manner can the most suitable temperatures for their decomposition be ascertained. Generally speaking, the more uniform the oil, both as regards the hydrocarbon series to which its constituents belong, and as regards boiling point, the better are the results which can be obtained, as it is then possible to adjust the temperature of the chequer work of the carburetter and superheater to that which is most suitable for the "cracking" of all the hydrocarbons. Such uniform oils would in most cases be too expensive for use; in the oils in common use, the boiling point of the bulk of the constituents varies usually from 250° to 400°. As the best cracking temperature for the various constituents differs, an average temperature has to be found in working which gives the best results from the oil as a whole. With a mixture containing oils from different series of hydrocarbons, the necessary variations of working temperature for the best results are much greater than with different hydrocarbons of the same series, on which account the mixing of oils of different origin in the storage tanks should be avoided as far as practicable.

In general, the only tests made of deliveries of such oil are its specific gravity at 60° F. (correction for each degree Fahrenheit below or above 60° =  $\pm 0.00036$ ), its flash point, and the percentage of residue (coke) remaining on complete distillation in a flask, which should not exceed 1 per cent., and is mostly much below this figure. The sulphur may also be determined, by Eschka's method (Vol. I, p. 245).

For a more complete examination, which is often desirable in the case of a new sample of oil, this may be distilled according to Engler's method (*cf.* Vol. III., under "Petroleum"), 100 c.c. of the oil being distilled in a fractionating flask of standard dimensions, at the rate of 2 to 3 c.c. per minute. The fractions are collected in weighed and graduated tubes, and the percentage of each fraction by weight and by volume, and its specific gravity determined. In addition, the colour of the fractions is noted, and also whether the higher fractions deposit solid hydrocarbons at 0° and at 15° respectively.

The portion boiling below 150° is known as *Light Oils*, that between 150° to 300° as *Burning Oils*, and that above 300° as *Heavy Oils*, but for the detailed examination of an oil it is usual to take a much larger number of fractions. A very usual method adopted in the United States, and also frequently in this country, is to take the fractions over each 50° F., but in this case an additional change of receiver is also made at 302° F. and 572° F. (150° and 300° C.) in order to express the percentages of light, burning, and heavy oils respectively. The figures given in the table below give the results obtained in the examination of a sample of gas oil in this manner.

### Analysis of Sample of Gas Oil.

*Colour and Appearance.*—Brown oil, with bluish fluorescence.

*Specific Gravity.*—At 60° F. 0.8886.

*Flash Point.*—203° F. *Water*, traces only.

*Suspended Matter.*—Nil. *Sulphur*, 0.17 per cent.

### Distillation Test.

Number of Fraction.	Boiling point. Degrees F.	Sp. gr. at 60° F.	Per cent. by volume.	Per cent. by weight.	Summary.
1	450 to 500	0.8676	23.3	22.74	Middle Oils 70.2 per cent. by vol.
2	500 „ 550	0.8819	36.1	35.78	
3	550 „ 572	0.8904	10.8	10.86	
4	572 „ 600	0.8944	9.8	9.83	Heavy Oils 29.5 per cent. by vol.
5	600 „ 650	0.8992	10.0	10.10	
6	650 „ 700	0.9094	5.6	5.79	
7	700 „ 750	0.9203	4.1	4.28	
8	Coke	...	...	0.30	



*Colour of Fractions.*—No. 1, colourless; Nos. 2 to 7, colour increasing from pale to full yellow. All fractions show bluish fluorescence.

*Condition of Fractions.*—All completely liquid at 60° F. and at 32° F.

*Sulphuretted Hydrogen.*—Evolved in very small quantity throughout distillation.

In addition to the specific gravity, Ross and Leather<sup>1</sup> recommend the determination of the refractive index of each fraction, as they find that for fractions of the same boiling point, the value for gas-making purposes increases with a decrease in the specific gravity and refractive index.

They also find that the following method of analysis gives comparative figures for oils which closely represent their value for carburetted water gas manufacture in actual practice. The oil is gasified in a small retort 9 ins. long by 5 $\frac{3}{4}$  ins. wide, and 4 $\frac{1}{4}$  ins. high, heated in a muffle furnace, the retort being fitted with an electrical pyrometer and two tubes, one just entering the retort for the introduction of the oil, and the other extending to the end of the retort for the delivery of the oil gas. As soon as the retort has reached the required temperature (which varied in the tests given between about 600° and 900° C.), the gas for heating is shut off, and 15 c.c. of the oil to be tested run in during a period of about three minutes, the gas evolved being passed through a wash-bottle to remove tar, collected in a small measuring holder, and the percentage of unsaturated hydrocarbons contained in it determined by absorption with fuming sulphuric acid. The figure representing the relative value of the oil is obtained by multiplying the number of cubic centimetres of gas produced from a given quantity of oil by the percentage of unsaturated hydrocarbons found. Comparison of the relative figures thus obtained from different oils with those obtained from the same oils in actual working on the large scale showed close agreement.

Mayer and Hempel,<sup>2</sup> in an exhaustive investigation of oils, find that their gas-making value may be suitably ascertained by the small scale distillation, the samples being allowed to drop slowly into an inclined iron tube heated by gas burners, and connected with apparatus for the collection of the tar and gas, the illuminating and calorific power of the latter being ascertained. The multiple of gas yield into illuminating power, and of gas yield into calorific power, at the optimum retort temperature, then give fairly representative values for the different oils. They further find that the optimum temperature is approximately the same for all types of oil examined, namely, about 750°, and that variations from the optimum lower the illuminating power multiple to a much greater extent than the calorific power multiple. Moreover, their

<sup>1</sup> *Analyst*, 1906, 31, 284; 1907, 32, 241.

<sup>2</sup> *J. Gasbeleucht.*, 1910, 53, 77, 101, 137, 155.

tests also show that the optimum temperature remains the same when the cracking of the oil is carried out in presence of large volumes of hydrogen and carbon monoxide, as is the case in the manufacture of carburetted water gas, in spite of the fact that in this case a considerable amount of combination takes place between the hydrogen and the unsaturated hydrocarbons present in the hot oil gas. When the cracking is carried out in presence of water gas, however, variations from the optimum temperature of  $750^{\circ}$  (from  $730^{\circ}$  to  $880^{\circ}$ ) have comparatively little effect on the calorific multiple, the loss of olefines at higher temperatures being largely counterbalanced by increased production of methane, ethane, etc. The illuminating multiple, on the other hand, which is much more directly dependent on the percentage of olefines, is very materially affected by deviations from the optimum temperature.

### C. OILS EMPLOYED FOR CARBURETTING IN THE COLD

In order to increase the illuminating power of the gas and to ensure its reaching the statutory quality, the addition of volatile hydrocarbons to the gas is frequently employed, although owing to the fast diminishing importance attached to illuminating power, the amount so used is steadily decreasing.

The hydrocarbons employed for this purpose are the lowest boiling fractions of petroleum (carburine, petrol) and crude benzol. The use of the former is, however, practically given up owing to the rise in price due to its increasing employment for internal combustion motors, the price of benzol having fallen at the same time.

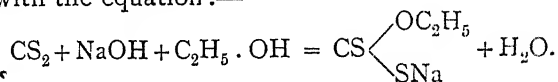
**1. Crude Benzol.**—The benzol usually employed consists of the so-called 90 per cent. benzol of the tar distillers—*i.e.*, a liquid of which 90 per cent. distils over below  $100^{\circ}$ . The compliance of the sample with this condition is tested by distilling 100 c.c. from a flask through a 3-bulb Le-Bel-Henninger fractionating column.

Some samples of crude benzol, however, contain considerable quantities of sulphur, chiefly as carbon bisulphide, and to a smaller extent as thiophene; these are objectionable, inasmuch as they increase the sulphur content of the purified gas.

*Determination of the Total Sulphur.*—Irwin's method may be adopted, which utilises the ordinary Referees sulphur test apparatus, employed for the estimation of sulphur in coal gas (see p. 669). The burner of the latter is replaced by a small spirit lamp, in which 10 c.c. of the benzol and 90 c.c. of alcohol are placed, and the mixture completely burned with a small flame under the trumpet tube of the apparatus, the flame being surrounded with lumps of ammonium carbonate. The sulphur is converted into ammonium sulphate, a solution of which collects in the receiver, and is precipitated at the

conclusion of the test as barium sulphate in the usual manner, and weighed.<sup>1</sup>

*Carbon Bisulphide.*—For the determination of carbon bisulphide alone, many methods have been proposed; the most convenient are those which depend on its conversion into a xanthate. For this purpose, 50 c.c. of the benzol is mixed with 50 c.c. of 10 per cent. alcoholic potassium or sodium hydroxide and allowed to stand for a short time, when the carbon bisulphide is converted into xanthate in accordance with the equation:—



Water is then added, the whole shaken, the lower aqueous layer removed by a separating funnel, and the benzene layer washed two or three times successively with small quantities of water; the combined washings are then made up to 500 c.c. An aliquot portion of the solution is acidified with acetic acid, and titrated with a solution of copper sulphate containing 12.475 g.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  per litre (1 c.c. = 0.0076 g.  $\text{CS}_2$ ). The xanthic acid is precipitated as cupric xanthate; the precipitation is complete when a drop of the clear solution gives a brown coloration with potassium ferrocyanide.

According to Harding and Doran,<sup>2</sup> the copper xanthate thus formed has not a constant composition and more accurate results are obtained by the following method:—The xanthate solution, after acidification, is precipitated with an excess of a decinormal solution of cupric acetate in dilute acetic acid, and allowed to stand for ten minutes; under these conditions, in presence of an excess of copper, the xanthate formed has a constant composition, the ratio  $\text{CuO}:\text{CS}_2$  being 1:1.925, or very nearly that required for cupric xanthate. The precipitate is filtered off, and the excess of copper in the filtrate determined by addition of potassium iodide, and titration with  $N/10$  sodium thiosulphate, the copper acetate solution being standardised in a similar manner. From the amount of copper precipitated and the above ratio of  $\text{CuO}:\text{CS}_2$ , the amount of the latter may be readily calculated.

The amount of sulphur in the xanthate solution may also be determined gravimetrically, by boiling the alkaline xanthate solution with pure hydrogen peroxide solution, whereby the xanthate is oxidised to sulphate which is determined with barium chloride in the usual manner.<sup>3</sup>

The quantity of carbon bisulphide in crude benzol may also be estimated by adding to 10 c.c. of the sample a few drops of phenylhydrazine, and allowing the mixture to stand for one to two hours, when the carbon bisulphide is precipitated as the crystalline compound

$\text{C}_6\text{H}_5\text{N}_2\text{H}_4\text{CS.SN}_2\text{H}_2\text{C}_6\text{H}_5$ , which is filtered off on a dried tared filter, washed with pure benzene, and dried in vacuo over sulphuric acid. The weight of precipitate found, multiplied by 0.26, gives the weight of carbon bisulphide.<sup>1</sup>

*Thiophene*.—According to Denigès,<sup>2</sup> the amount of this substance may be determined by adding 2 c.c. of the benzol to 20 c.c. of a solution obtained by dissolving 50 g. of mercuric oxide and 200 g. of pure sulphuric acid in 1 litre of water, and heating the mixture at 100° in a stoppered bottle for fifteen minutes, with occasional shaking. The precipitate formed is filtered off on a weighed filter; the weight obtained, multiplied by 0.0758, gives the weight of thiophene.

**2. Oil Gas Condensate.**—The liquid hydrocarbons which separate when oil gas is compressed, are also used for enrichment purposes, being sold usually under special trade names. The bulk of this oil consists of benzene, which is usually present to the extent of some 70 per cent.; of the remainder, some 15 per cent. consists of toluene, 5 per cent. of higher boiling aromatic hydrocarbons, and about 10 per cent. of olefines. Its enrichment effect averages from 90 to 95 per cent. of that of commercial 90 per cent. benzol.

For its examination, it is usual to distil 100 c.c., using a 3-bulb fractionating column, and to ascertain the volume of distillate for each interval of 5°. The percentage of olefines is estimated from the quantity of bromine with which it combines, in the following manner:—A solution of bromine in dried carbon bisulphide is made up of about decinormal strength, and 25 c.c. of this solution added to about 0.5 g. of the oil dissolved in dried carbon bisulphide and contained in a stoppered bottle. If the solution is not then strongly coloured by unaltered bromine, a further 25 c.c. of bromine solution is added. After standing for fifteen minutes in the dark, a solution of potassium iodide is added, the bottle vigorously shaken, and the liberated iodine estimated by titration with *N*/10 sodium thiosulphate and starch, the bottle being well shaken between each addition of thiosulphate. The bromine solution is standardised in a similar manner, and from the results of the two titrations, the amount of bromine absorbed is calculated; 1 c.c. of *N*/10 thiosulphate = 0.008 g. Br.

As an example, the following test may be given:—

25 c.c. bromine solution	= 24.4 c.c. <i>N</i> /10 thiosulphate.
Weight of oil taken	= 0.534 g.
Bromine solution added	= 25 c.c.
<i>N</i> /10 thiosulphate required after 15 min.	= 10.2 c.c.
Per cent. of bromine absorbed	= $\frac{(24.4 - 10.2) \times 0.008}{0.534}$

Assuming that the average composition of the olefines present is  $C_6H_{12}$ , 84 parts of such olefines combine with 160 parts of bromine, and the approximate percentage of olefines is therefore :—

$$\frac{84 \times 21.3}{160} = 11.2 \text{ per cent.}$$

### III.—GAS ANALYSIS<sup>1</sup>

#### A. GENERAL CONSIDERATIONS ON VOLUMETRIC GAS ANALYSIS

The constituents of a gaseous mixture which are present in considerable amount are usually determined by volumetric methods, whilst those present only in small quantity are estimated either by gravimetric or volumetric methods (*cf.* III., E., p. 659).

The scientific foundations of the methods of volumetric gas analysis were laid by Bunsen, who embodied his classical researches on the subject in his work on "Gasometry" (1857). The methods adopted by him have since been considerably amplified by numerous other workers, and at the same time have been rendered more available for technical work by the construction of apparatus specially suitable for this purpose, in which greater rapidity is obtained without material sacrifice of accuracy.

The most important types of apparatus and methods of working are described in the section on Technical Gas Analysis (Vol. I., pp. 189 *et seq.*); this section accordingly includes only such data as are necessary to amplify the information there given to suit the special requirements of gasworks.

The chief types of gaseous mixtures which are met with in gasworks' practice are given in the following table, together with their approximate average percentage composition; it is to be remembered, however, that the percentages of the various constituents may vary somewhat widely from those given as an average in the table :—

	H.	CH <sub>4</sub> .	CO.	C <sub>n</sub> H <sub>m</sub> .	CO <sub>2</sub> .	O.	N.
Oil gas . . . . .	8	52	14	25	...	...	1
Carburetted water gas . . . . .	37	13	33	9	4	0.4	4
Coal gas . . . . .	50	30	8	3.5	1.5	0.5	6.5
Blue water gas . . . . .	50	1	40	...	4	...	5
Generator gas . . . . .	10	0.5	27	...	6	...	56
Waste gases . . . . .	?	...	?	...	21	21	< 79

Apart from the value of a complete gas analysis in the investigation of the nature of the changes taking place in the various processes, and the effect of altered conditions on the working, the information gained

<sup>1</sup> *cf.* Vol. I., Section on Technical Gas Analysis, pp. 189-240.

from such analysis is in many cases useful for (1) the valuation of the gas from the amount of each constituent present; (2) the calculation of its calorific power; (3) the calculation of the amount of air required for its complete combustion; (4) the calculation of the theoretical flame temperature.

The method of gas-volumetric analysis depends in the first place on the successive removal of single constituents by treating the gas with suitable absorbing agents, and measuring the resulting diminution of volume. Carbon dioxide, heavy hydrocarbons, and oxygen are almost always estimated in this manner; carbon monoxide is usually estimated by absorption, and occasionally also hydrogen. Where no suitable absorbent is known, as with methane, and also usually with hydrogen, and sometimes with carbon monoxide, these constituents are determined by combustion, their quantities being deduced from the relation of the contraction on combustion and the volume of carbon dioxide produced, to the original volume. The residual incombustible gas is taken as nitrogen.

#### B. ESTIMATION OF GASES BY ABSORPTION

In estimating gases by absorption, two general types of apparatus are employed. In the one, represented by the Frankland-Macleod apparatus and its modifications and the Bunte burette, small quantities of fresh absorbent material are used for each determination; in the second class, represented by the Hempel and the Orsat apparatus, the gas is passed from the measuring vessel into an absorption pipette containing a large volume of the absorbent material, and then transferred back to the measuring vessel, the same quantity of absorbent being used for a large number of absorptions.

The absorption pipettes employed by Hempel and Orsat are fully described in Vol. I., pp. 198 *et seq.* Pfeiffer employs a modified form of the Hempel pipette, which permits of the replacement of the gas in the capillary connecting tube by means of water. This modification is shown in Fig. 90, the capillary side tube, *c*, being connected to the

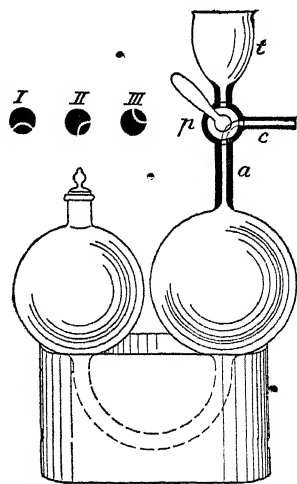


FIG. 90.

burette; by altering the position of the stopcock, *p*, in a manner which can be readily seen from the diagram, water may be run from the funnel, *t*, into the capillary, *c*, and the air expelled before connecting with the burette; and when drawing the gas back to the burette after absorption, the absorbing liquid is allowed to rise only to the stopcock,

*p*, after which, by turning the latter through an angle of  $90^\circ$ , water is run from the funnel, *z*, to the capillary, *c*, the gas remaining in which is thus forced into the burette; this operation is carried out before each reading. In place of the wooden or metal stand used by Hempel, the tube is bedded in a sheet-metal case by means of paraffin wax or plaster of Paris.

The absorbents most commonly in use for the various constituents are given under the respective gases.

(*a*) **Sulphuretted Hydrogen**.—When this gas is present in considerable quantity, as is the case with crude coal gas, it may be estimated volumetrically with a fair degree of accuracy by the employment of a slightly acid, 10 per cent. solution of cadmium chloride or sulphate, as absorbent. Contact with the solution for one minute is sufficient for complete elimination of the sulphuretted hydrogen; shaking is unnecessary and inadvisable, as it tends to effect the absorption of other constituents.

(*b*) **Carbon Dioxide**.—The absorbent mostly employed is a solution of one part of potassium hydroxide in two parts of water. Contact for one minute is sufficient for complete absorption.

When the gases also contain hydrocarbon vapours, as is the case with coal gas, carburetted water gas, and oil gas, there is a tendency on the part of the potassium hydroxide solution, especially when a large volume of it is used, to absorb, in addition, some of these vapours (chiefly benzene and smaller quantities of its homologues). The error due to this absorption may bring the carbon dioxide from 0.1 to 0.4 per cent. too high, and consequently the unsaturated hydrocarbons too low by a corresponding amount. In such cases, it is advisable to use a more dilute potassium hydroxide solution (one part of potassium hydroxide to three parts of water), in which case, provided the gas is not shaken with the reagent, very little absorption of vapours occurs.

(*c*) **Total Unsaturated Hydrocarbons**.—These hydrocarbons consist chiefly of ethylene and benzene vapour, but usually small amounts of their homologues are also present; as a rule, these constituents are determined together, by absorption with either fuming sulphuric acid, or with bromine water.

With the former reagent, shaking must be continued for three to five minutes to effect complete absorption, and before remeasuring, the gas must be passed over potassium hydroxide solution to remove the vapours of sulphur dioxide, etc. Where a large bulk of fuming acid is employed, as in the Hempel apparatus, oxygen, if present, is absorbed to a small extent, probably by the compounds formed from the hydrocarbons and sulphuric acid; it should, therefore, be removed from the gas before the absorption with fuming sulphuric acid.

The absorption with bromine is carried out with a solution of

bromine in water or in potassium bromide solution. The olefines are very rapidly converted into the dibromides, but the aromatic hydrocarbons are not chemically acted on by the bromine, their removal being simply mechanical; a period of three minutes should be allowed for their absorption. Before remeasuring, the gas must be treated with potassium hydroxide to remove the excess of bromine vapour.

The separate determination of olefines and of benzene and its homologues by special absorbents has frequently been proposed, but most of the methods have been shown to be quite unreliable. Recently, Dennis and O'Neill found that benzene vapour might be estimated by absorption with an ammoniacal nickel nitrate solution, but subsequent investigation has shown that this is only the case when the gas analysed also contains hydrocyanic acid, the compound formed being  $C_6H_6$ ,  $NH_3$ ,  $Ni(CN)_2$ . Dennis and M'Carthy<sup>1</sup> have recommended an ammoniacal solution of nickel cyanide for the absorption, prepared as follows:—A solution of 25 g. of potassium cyanide in 25 c.c. of water is added to a solution of 50 g. of crystallised nickel sulphate in 75 c.c. of water, 125 c.c. of ammonia (sp. gr. 0.91) added, the whole cooled to  $0^\circ$ , and poured off from the separated potassium sulphate; 18 g. of citric acid in 10 c.c. of water are then added, the solution again cooled to  $0^\circ$  for ten minutes, decanted from potassium sulphate crystals, and a few drops of benzene then added and shaken till combination takes place, as the solution is much more active after it has absorbed some benzene. The gas must be well shaken with the reagent for at least three minutes, and before remeasuring must be passed into dilute sulphuric acid to remove ammonia. The solution has no action on ethylene or on carbon monoxide; the former may be estimated by absorption with bromine or fuming sulphuric acid after the removal of the benzene. The small quantities of benzene homologues present would, however, not be absorbed by the ammoniacal nickel cyanide, but their amount rarely exceeds 0.1 per cent. Check tests given by Dennis and M'Carthy show good agreement with the theoretical figures, but a wider experience with varied gases is necessary to establish the general applicability of the method.

(d) **Oxygen**.—The absorbents employed are alkaline pyrogallol, phosphorus, and sodium hydrosulphite, the preparation and employment of which is described in Vol. I., p. 209.

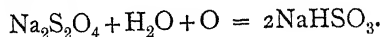
The pyrogallol solution is prepared by mixing 1 volume of aqueous pyrogallol (1:3) with 5 volumes of aqueous potassium hydroxide (3:2).

The sodium hydrosulphite solution is made by dissolving 50 g. of the salt in 250 c.c. of water and adding 40 c.c. of a sodium hydroxide solution containing 500 g. of alkali to 700 c.c. of water, and is used in a

<sup>1</sup> *J. Amer. Chem. Soc.*, 1908, 30, 233.



pipette filled with rolls of iron-wire gauze. The absorption takes place according to the equation:—



When both unsaturated hydrocarbons and oxygen are present, as is the case in illuminating gas, the order in which these are absorbed varies according to the absorbents employed. If alkaline pyrogallol be used, the oxygen determination should precede that of the hydrocarbons, as the fuming sulphuric acid which has already absorbed hydrocarbons tends to absorb some oxygen, but at the same time the use of the strongly alkaline pyrogallol before removal of hydrocarbon vapours tends to absorb some of the latter, thus making the oxygen too high and the unsaturated hydrocarbons too low. When phosphorus is used for estimating oxygen, it is essential that the unsaturated hydrocarbons be first removed, as mere traces of ethylene entirely prevent the absorption of oxygen by phosphorus; owing to the above-mentioned absorption of oxygen by fuming sulphuric acid, it is necessary in this case to employ bromine for the absorption of the hydrocarbons. The use of bromine, with the subsequent use of phosphorus for the absorption of oxygen, gives the most accurate results, and, provided the gas measuring burette is water-jacketed, the percentage of oxygen is then given correctly in almost all cases to within 0.1 per cent., as has been shown by a long series of tests in which coal gas, free from oxygen, was mixed with known volumes of air and analysed by this method (Colman).

(e) **Carbon Monoxide.**—The absorbent solution used for this constituent is either an acid or ammoniacal solution of cuprous chloride; the latter solution is most frequently employed. Oxygen and ethylene are absorbed by the acid solution, and acetylene, in addition, by the ammoniacal solution; these constituents must, therefore, be removed before the estimation of the carbon monoxide.

The acid solution is prepared by dissolving 100 g. of crystallised cupric chloride in 500 c.c. of concentrated hydrochloric acid diluted with an equal volume of water, and allowing the solution to stand with an excess of metallic copper until colourless.

For the ammoniacal solution required in the Hempel or Orsat apparatus, a very active solution is obtained by Winkler's method of preparation. A stock solution is made up by dissolving 200 g. of cuprous chloride, and 250 g. of ammonium chloride in 750 c.c. of water; this solution is kept in a bottle closed with a rubber stopper, into which a few spirals of copper wire are also placed. When required for use this solution is mixed with one-third of its volume of ammonium hydroxide of sp. gr. 0.905.

For use in apparatus in which only a small volume of the reagent

is employed, Bone recommends the following method of preparation. Fifty to seventy grams of white cuprous chloride are suspended in 250 c.c. of water containing 10 to 15 g. of ammonium chloride, and ammonia gas passed into the liquid (air being excluded) until no more solid dissolves and the solution smells distinctly of ammonia. A further quantity of about 5 g. of cuprous chloride is then added, the liquid well shaken, and stored in bottles closed with a rubber stopper; after a few hours the solution should cease to smell of ammonia.

Solutions which have absorbed carbon monoxide give off some of the gas to indifferent gases, an equilibrium being always obtained for the carbon monoxide content between the gas and the liquid. For the complete removal of the carbon monoxide from the gas, the latter must, therefore, eventually be treated with a solution containing very little absorbed gas. Where small quantities of the reagent are employed, two absorptions with different portions of the fresh solution are always used; with the Hempel apparatus two absorption pipettes are used in succession, the second containing solution which has absorbed only small quantities of carbon monoxide. As soon as the treatment in the second pipette shows an absorption of more than 0.4 to 0.5 per cent., the first pipette is recharged with fresh solution and used for the final absorption, the pipette previously used for this purpose being then employed for the first absorption.

(f) **Hydrogen.**—This gas is almost always determined by combustion, but occasionally Hempel's method of absorption by palladium is employed (Vol. I., p. 212). Paal and Hartmann<sup>1</sup> have recently shown that hydrogen may also be determined by absorption with a solution prepared by dissolving 2.22 g. of colloidal palladium<sup>2</sup> (containing 67.36 per cent. = 1.5 g. Pd) and 2.74 g. of sodium picrate in 125 c.c. of water, the solution being placed in a Hempel or similar pipette. The absorption is somewhat slow, requiring from ten to twenty minutes, with occasional shaking. Carbon dioxide, heavy hydrocarbons, oxygen, and carbon monoxide must be previously removed. Sulphur, phosphorus, and arsenic compounds, which destroy the catalytic power of the palladium, are simultaneously removed by the usual absorption reagents for these constituents.

When the solution becomes inactive, the palladium may be recovered by carefully adding dilute sulphuric acid, drop by drop, so long as a precipitate forms, avoiding an excess. The precipitated palladium is filtered, washed, suspended in a small quantity of water, dissolved by gradual addition of sodium hydroxide solution, and sodium picrate again added.<sup>3</sup>

<sup>1</sup> *Ber.*, 1910, 43, 243.

<sup>2</sup> This is supplied by Kalle & Co., Biebrich am Rhein.

<sup>3</sup> Brunck, *Chem. Zeit.*, 1910, 34, 1313, 1332.

## C. ESTIMATION OF GASES BY COMBUSTION

Of the combustible gases, methane and ethane are always estimated by combustion, and in most cases the estimation of hydrogen, and often that of carbon monoxide, is carried out in this way. The usual method is to admit either oxygen or air and to burn the gases, either by explosion, or by slow combustion over heated metals of the platinum group, whereby hydrogen, either free or combined with carbon, is converted into liquid water, whilst the carbon is oxidised carbon dioxide.

## 1. CHANGES IN VOLUME BY COMBUSTION

The volume of combustible gases to be estimated stands in a certain relation to the contraction in volume resulting from the combustion (C), to the carbon dioxide formed on combustion ( $\text{CO}_2$ ), which can easily be determined by absorption, and to the sum of the hydrogen contraction plus carbon dioxide (total contraction C). The volumetric relations are shown in the following table. In the graphic representation of the volume changes, the squares enclosed by dotted lines denote the volumes which disappear by contraction, and the darkened squares the carbon dioxide formed by combustion.

	Combustion formulæ.	Graphic representation.	The contrac- tion, c.	Corresponds to	Therefore	1 Vol. CO <sub>2</sub> equal to	Total contraction (C+CO <sub>2</sub> ).	In terms of total contrac- tion, C.
Hydrogen.	$2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ 2 Vol. 1 Vol. 0 Vol. 3 Vol.		3 Vol.	2 Vol. H	$\frac{2}{3}\text{C}$ = H	...	3 Vol.	$\frac{2}{3}\text{C} = \text{H}$
Carbon Monoxide.	$2\text{CO} + \text{O}_2 = 2\text{CO}_2$ 2 Vol. 1 Vol. 2 Vol. 3 Vol.		1 Vol.	2 Vol. CO	$2\text{C}$ = CO	1 Vol. CO	3 Vol.	$\frac{2}{3}\text{C} = \text{CO}$
Methane.	$\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$ 1 Vol. 2 Vol. 1 Vol. 0 Vol. 3 Vol. 1 Vol.		2 Vol.	1 Vol. CH <sub>4</sub>	$\frac{1}{2}\text{C}$ = CH <sub>4</sub>	1 Vol. CH <sub>4</sub>	3 Vol.	$\frac{1}{3}\text{C} = \text{CH}_4$

Hence the volumes are as follows:—

$$\begin{aligned}\text{H} &= \frac{2}{3}\text{C} \text{ (or } \frac{2}{3}\text{C)} \\ \text{CO} &= \text{CO}_2, \text{ or } 2\text{C}, \text{ or } \frac{2}{3}\text{C} \\ \text{CH}_4 &= \text{CO}_2, \text{ or } \frac{1}{2}\text{C}, \text{ or } \frac{1}{3}\text{C}.\end{aligned}$$

If only one of the combustible gases be present in the mixture, there is, in the case of carbon monoxide and of methane, a choice in deducing their volumes, namely, either from the contraction  $c$ , due to the carbon dioxide formed on combustion, or from the total contraction  $C$ . As will be readily understood, the latter gives the more accurate results chiefly because of the larger volume readings that enter into the calculation.

### Gaseous Mixtures with Two or Three Combustible Gases.

In this case, the calculation is more complex. If methane and carbon monoxide are both present, neither of them alter their volume by oxidation to carbon dioxide, so that the following relation holds:—

$$1 \text{ vol. CO}_2 = 1 \text{ vol. CO, or } 1 \text{ vol. CO}_2 = 1 \text{ vol. CH}_4.$$

A contraction results, however, owing to the oxygen taken up in the combustion, which must be subtracted from the contraction  $c$ , to obtain the nett contraction due to hydrogen.

(a) **Hydrogen and Carbon Monoxide.**—To the volume of carbon monoxide as ascertained (= vol. of  $\text{CO}_2$  formed) there corresponds a contraction, due to the disappearance of oxygen, equal to half the volume of the  $\text{CO}_2$ . This must be subtracted from the contraction  $c$ , as found, in order to obtain the contraction due to hydrogen. The volumetric relations are therefore:—

$$\begin{aligned} \text{CO} &= \text{CO}_2 \\ \text{and } \text{H} &= (c - \frac{1}{2}\text{CO}_2)^{\frac{2}{3}}. \end{aligned}$$

*Example* (Mixture of Hydrogen, Carbon Monoxide, and Nitrogen):—

Volume of Gas mixture	=	21.1 c.c.
„ Air added	=	97.5 „
Total	.	<u>118.6 c.c.</u>

After combustion = 102.1 c.c.; contraction  $c$  = 16.5 c.c.; H = 9.53 c.c.

After  $\text{CO}_2$  absorption = 97.7 c.c.; carbon dioxide = 4.4 c.c.; CO = 4.4 c.c.

If, after absorbing the  $\text{CO}_2$  formed in the combustion, the total contraction  $C$  (=  $c + \text{CO}_2$ ) be considered, the volume of CO, of course, remains the same (= vol. of  $\text{CO}_2$ ).

On the other hand, the volume of:—

$$\text{H} = \frac{2}{3}C - \text{CO}_2.$$

Since, according to the first equation,

$$\text{H} = (c - \frac{1}{2}\text{CO}_2)^{\frac{2}{3}}$$

$$\text{now } C = c + \text{CO}_2$$

$$\text{and } c = C - \text{CO}_2$$

$$\therefore \text{H} = (C - \text{CO}_2 - \frac{1}{2}\text{CO}_2)^{\frac{2}{3}} = (C - \frac{3}{2}\text{CO}_2)^{\frac{2}{3}} = \frac{2}{3}(C - \text{CO}_2).$$

Applying this to the example:—

Contraction	=	16.5 c.c.	
Carbon dioxide	=	$\frac{4.4}{20.9}$ "	CO = 4.4 c.c.
Total contraction C	=	<u>20.9 c.c.</u>	H = 9.53 "

In mixtures containing hydrogen accompanied by either carbon monoxide or methane, provided that the total volume  $V$  of the combustible gases is known, the calculation on the basis of the foregoing is much simplified, since the volume of carbon monoxide or methane is equal to the ascertained volume of carbon dioxide, whilst the difference is due to hydrogen:—

$$\begin{aligned} \text{CO or CH}_4 &= \text{CO}_2 \\ \text{H} &= V - \text{CO}_2. \end{aligned}$$

(b) **Hydrogen, Carbon Monoxide, and Methane.**—The volume of these constituents can be calculated if their total volume  $V$  (combustible portion), is known, a value which, in technical gas mixtures, is obtained from the estimation of the accompanying ingredient, nitrogen. The calculation starts from the known nitrogen content,  $N_1$  of the air added for the combustion—*i.e.*, the volume of air  $\times 0.7905$ . After combustion, followed by the absorption of the carbon dioxide, and of the excess of oxygen added from the air, there remains a volume of nitrogen,  $N_2$ , which is at least as large as  $N_1$ . The difference,  $N_2 - N_1$ , gives the nitrogen,  $N$ , present in the original volume taken,  $R$ , whence the volume of the combustible gases is:—

$$V = R - N.$$

It then follows, as already shown:—

$$\begin{aligned} \text{further,} \quad \text{H} &= V - \text{CO}_2, \\ \text{and} \quad \text{CO} &= \frac{1}{3}\text{CO}_2 + V - \frac{2}{3}\text{C} \\ \text{CH}_4 &= (\text{CO}_2 + c)\frac{2}{3} - V. \end{aligned}$$

Starting again from the total contraction  $C$ , and substituting the equivalent value  $(C - \text{CO}_2)$  for  $c$  in the above equation, the following simplified equations are obtained:—

$$\begin{aligned} \text{H} &= V - \text{CO}_2 \\ \text{CO} &= \text{CO}_2 + V - \frac{2}{3}\text{C} \\ \text{CH}_4 &= \frac{2}{3}\text{C} - V. \end{aligned}$$

Or, by adopting the following notation,

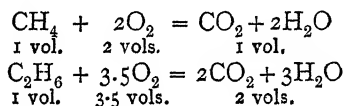
- Volume I. = Gas residue (R) + air.  
 " II. = Residue after explosion.  
 " III. = Residue after explosion and absorption of  $\text{CO}_2$ .  
 " IV. = Residue after absorption of the excess O.

Then :—

$$\begin{array}{rcl}
 \text{C} & = & \text{Vol. I-III.} \\
 \text{CO}_2 & = & \text{,, II-III.} \\
 \text{N}_2 & = & \text{,, IV.} \\
 \text{N} & = & \text{N}_2 - \text{N}_1 \text{ (N}_1 = \text{air} \times 79.05). \\
 \bullet \text{V} \bullet & = & \text{R} - \text{N.}
 \end{array}$$

(c) **Methane and Ethane.**—When the gaseous mixture contains higher homologues of methane, of which the only one commonly met with in any quantity is ethane, calculations are more complex. In the case of a mixture of hydrogen, methane, and ethane remaining with the nitrogen after the absorption of the other constituents, including carbon monoxide, a value for ethane may be calculated from the volume of carbon dioxide produced, the contraction and the volume of oxygen absorbed on explosion, but the results are not very reliable. If, however, the hydrogen be also absorbed by Paal's colloidal palladium solution (p. 637), leaving only methane and ethane (and nitrogen), the volumes of methane and ethane may be found from the volume of carbon dioxide produced and the contraction, C.

From the equations :—



it follows that methane gives its own volume of  $\text{CO}_2$  and a total contraction of twice its volume, whilst ethane gives twice its volume of  $\text{CO}_2$  and a total contraction of 2.5 times its volume. If  $x$  and  $y$  represent the volumes of methane and ethane respectively, then :—

$$\begin{array}{l}
 x + 2y = \text{vol. CO}_2 \text{ formed (CO}_2\text{)} \\
 2x + 2.5y = \text{Contraction (C).}
 \end{array}$$

Hence,

$$\begin{array}{l}
 \text{CH}_4 = \frac{4}{3}(\text{CO}_2 - \frac{1}{2}\text{C}). \\
 \text{C}_2\text{H}_6 = \frac{2}{3}(2\text{C} - \text{CO}_2).
 \end{array}$$

In the case of coal gas with the carbonising temperatures now usually employed, very little, if any, ethane is generally present, but with lower carbonising temperatures, and also with oil gas and carburetted water gas, appreciable amounts of ethane are mostly contained in the gas.

## 2. METHODS OF COMBUSTION

(a) **Explosion.**—In most cases the simplest, though not always a practicable method of combustion, consists in the explosion of the combustible mixture either with pure oxygen or with air. As the explosion vessel, either a measuring burette, provided with platinum electrodes, is used, or a special explosion pipette (*cf.* Vol I., pp. 213 and 222). Water

is quite unsuitable as the confining liquid, if the carbon dioxide formed has to be determined, as is usually the case, because under the high pressure of explosion a portion of this gas is absorbed; in most forms of gas analysis apparatus the combustion is effected over mercury.

The explosion pipette, filled with water, devised by Pfeiffer (Fig. 91) obviates the absorption of the carbon dioxide in the following way. The liquid (0.1 per cent. sulphuric acid) in the explosion bulb A is drawn over into B before explosion; two stopcocks, *a* and *b*, are provided for this purpose.

This pipette is particularly suitable to the analysis of coal gas by Pfeiffer's method (*cf.* p. 648); it is of much smaller capacity than other forms of explosion pipettes, but is sufficiently large to take one filling of the burette with air quite conveniently in addition to the combustible gas residue. The provision of the stopcock *a*, at the entrance to the bulb, instead of the customary rubber tubing and clip, protects the apparatus from risks due to back pressure to which the latter is exposed, and in this respect the smaller capacity is also an advantage. By fixing the platinum electrodes in the position shown, the formation of drops of liquid between the points is avoided.<sup>1</sup>

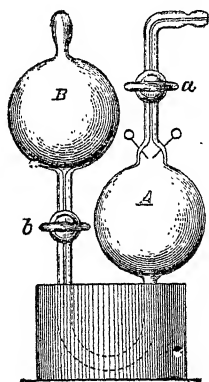


FIG. 91.

The liquid is drawn into the bulb B, by means of a piece of rubber tubing 20 cm. long attached to the end of the bulb. Too large an excess of oxygen or air should not be used for the combustion. In calculating roughly beforehand the quantities necessary, the ratios given on p. 638 are to be borne in mind, viz. :—

One vol. hydrogen requires  $\frac{1}{2}$  vol. oxygen, or approximately 2.5 vols. air.

One vol. carbon monoxide requires  $\frac{1}{2}$  vol. oxygen, or approximately 2.5 vols. air.

One vol. methane requires 2 vols. oxygen, or approximately 10.0 vols. air.

Below certain limits, however, small quantities of these gases in presence of comparatively large quantities of indifferent gas do not undergo combustion. Under these circumstances explosion can only be effected by the addition of oxygen, and in very unfavourable conditions it may even be necessary to add electrolytic gas in order to secure an explosive mixture. In practical work this complication has rarely to be resorted to, as the difficulty can be overcome by simpler methods, which will be explained subsequently.

On the other hand, in dealing with highly explosive mixtures, the nitrogen in the gases may also be oxidised, as was first pointed out by

<sup>1</sup> Cf. *Chem. Zeit.*, 1904, 28, 636. The pipette is supplied by H. H $\ddot{u}$ bold, Magdeburg.

Bunsen. Bunsen's experiments had reference only to admixtures of electrolytic gas and nitrogen, but he concluded that in order to avoid the oxidation of the nitrogen in the combustion of gaseous mixtures generally, not more than 26 to 64 vols. of combustible gas (inclusive of the necessary oxygen) should be present for every 100 vols. of incombustible mixture. These ratios form a satisfactory guide in the analysis of coal gas.

(b) **Combustion without Explosion by means of Palladium.**—Hydrogen and carbon monoxide are easily oxidised with air when passed over heated palladium; methane does not take part in the combustion so long as the temperature is not raised too high.<sup>1</sup> The method is, therefore, to be recommended for the estimation of hydrogen and carbon monoxide in the presence of methane (fractional combustion); it gives satisfactory results with small amounts of these gases in the presence of large quantities of indifferent gases. The palladium is used either in the form of wire or of palladium asbestos, and is placed in a small capillary glass tube which is interposed between the measuring burette and a pipette filled with water or a second burette (*cf.* Vol. I., p. 211). The mixture to be burnt is passed over the heated



FIG. 92.

palladium, and the contraction, and the carbon dioxide formed by combustion measured.

Palladium wire, first recommended by Bunte,<sup>2</sup> is used in the form of a very thin filament, about 1.5 cm. long, bent in two, and placed in the middle, narrowed portion of a tube of potash glass (Fig. 92); the wider parts of the tube are lightly stopped with asbestos fibre as a security against a possible explosion. The palladium is heated either by a spirit lamp or by a very small gas burner. According to Richardt,<sup>3</sup> the heating must only be carried so far that the tip of the flame begins to be coloured yellow by the sodium of the glass; if this condition be fulfilled, the combustion of methane does not take place (*cf.* p. 645).

Palladium asbestos, which was introduced by C. Winkler for fractional combustion, is prepared in the following way. Palladium chloride, obtained from 1 g. of palladium, is reduced by the addition of a few cubic centimetres of a cold, saturated solution of sodium formate, and sufficient sodium carbonate to make it strongly alkaline, and about 1 g. of best, long-fibred asbestos is placed in the solution; this should absorb all the liquid. The damp mass is allowed to dry at a gentle heat, and in this way palladium in a very fine state of division is precipitated on the

<sup>1</sup> *Cf.* H. G. Denham, *J. Soc. Chem. Ind.*, 1905, 24, 1202, and Vol. I., p. 211.

<sup>2</sup> *J. Gasbeleucht.*, 1878, 21, 263.

<sup>3</sup> *Ibid.*, 1904, 47, 592.



fibres, and adheres well to them even when thoroughly dried on the water-bath; the asbestos is finally washed with boiling water and again well dried. The combustion capillary, which is from 5 to 10 cm. long, and about 1 mm. internal and 5 mm. external diameter, is filled by moistening a few threads of the asbestos with water, twisting them together on a piece of filter paper, and then sliding a piece about 1 cm. long into the middle of the tube; the capillary is then dried on the water-bath.

The combination of the oxygen with hydrogen or with carbon monoxide takes place more readily by means of palladium asbestos than with palladium wire. If the gas be passed sufficiently quickly through the tube after the combustion has been started, the oxidation continues without further heating, and is rendered evident by the glowing of the end of the asbestos thread next to the entering gases.

(c) **Combustion of Methane by means of Platinum without Explosion.**—Methane is completely oxidised when passed with oxygen over brightly glowing platinum. Upon this fact Coquillion<sup>1</sup> based a method for the estimation of marsh gas in fire damp; the gas is passed over a platinum wire kept at a red heat by an electric current and placed in a vessel connecting the measuring burette with the absorption bulb for the carbon dioxide. C. Winkler's modified form of the Hempel pipette<sup>2</sup> is more generally useful. The lower neck of the pipette carries a rubber stopper with two holes through which pass two strong brass rods carrying at their lower ends binding screws for conducting the electric current. The upper ends of the rods are connected by a platinum wire 0.35 mm. thick forming a spiral of 6 turns 1.3 mm. wide; water is used as the confining liquid. The combustion is started by closing the circuit as soon as the gas and air mixture begins to pass out of the burette into the combustion chamber; as soon as the water level is depressed below the platinum spiral, the reaction takes place quietly and without danger. A disadvantage of this method is the necessity of having a battery, but in many cases the current from an ordinary lighting supply can be used. If the current is too strong the spiral soon melts, and if too weak the combustion of the methane is incomplete.

These inconveniences are avoided in the platinum capillary tube devised by Drehschmidt<sup>3</sup> (Fig. 93). This consists of a seamless platinum tube about 20 cm. long, 2 mm. thick, and 0.7 mm. internal diameter, and containing 3 or 4 pieces of thin platinum wire; brass connections are soldered to the ends of the tube for connecting to the measuring burette and pipette. Two small cooling cylinders, also made of brass, are fixed on to the brass tubes just above the bends, as shown. Before use, the soundness of the tube is tested by first heating it

<sup>1</sup> *Comptes rend.*, 1877, 84, 458.

<sup>2</sup> *Z. anal. Chem.*, 1889, 28, 286.

<sup>3</sup> *Ber.*, 1887, 21, 3245; cf. Vol. I., p. 214.

strongly, then closing one end and introducing compressed air at the other end (pressure=about 0.3 m. mercury); if the tube be then immersed in water any leakage is shown by air-bubbles rising.

To carry out the combustion, the tube is heated to a bright red heat by a broad, fan-shaped Bunsen flame; the combustion is complete after passing the mixture backward and forward twice. Explosions do not occur even when the mixture approaches the composition of electrolytic gas, nor does any diffusion of hydrogen take place through the walls of the heated tube.

By means of the methods of combustion described, the volume of the three combustible gases, hydrogen, carbon monoxide, and methane can be ascertained in four different ways:—

I. By a single combustion (either by explosion or by means of the platinum capillary), and calculating the different ingredients from the data  $V$ ,  $C$ , and  $CO_2$ , as described on p. 640.

II. By first burning hydrogen and carbon monoxide over heated palladium and thus estimating their volumes, and then oxidising the residual methane by itself in the platinum capillary and ascertaining its volume from the total contraction.

III. By determining hydrogen and carbon monoxide by burning a portion of the mixture over palladium, and exploding another portion to find the total contraction  $C$ , then:—

$$CH_4 = (C - \frac{2}{3}H + \frac{2}{3}CO) \frac{1}{3}.$$

IV. By first removing carbon monoxide by absorption with cuprous chloride, and then determining the hydrogen and methane either by explosion or by fractional combustion.

(*d*) **Combustion with Copper Oxide.**—This method, which is due to Jaeger,<sup>1</sup> depends on the fractional combustion of the mixture of gases over copper oxide at varying temperatures. As the oxygen required for the combustion is not added in the gaseous form, the relations of the volume changes are very simple; thus, the hydrogen disappears completely on burning and its volume is equal to the contraction, whilst the methane forms an equal volume of carbon dioxide, which is easily measured by absorption. The copper oxide is placed in a small tube of the form shown in Fig. 94, which is made of hard Jena glass with a capillary on one side and a somewhat wider tube on the other. To fill the tube, large-grained copper oxide is introduced, so that it lies at the beginning of the capillary, and a plug of asbestos fibre placed against it; the wide part of the tube is then filled with freshly ignited, powdered copper oxide, which is kept in position by a second plug of asbestos.

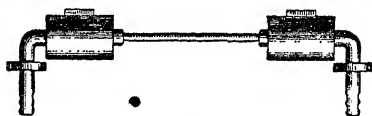


FIG. 98.

<sup>1</sup> *J. Gasbeleucht.*, 1898, 41, 764.

The tube is connected by rubber tubing on one side with the measuring burette, and on the other side with the absorption pipette charged with potassium hydroxide solution. For the combustion of the hydrogen the tube is heated to  $250^{\circ}$ ; this temperature is controlled by means of a thermometer, the bulb of which is placed close against the tube. After oxidising the hydrogen and reading the contraction, the thermometer is removed and the methane then oxidised by heating the copper oxide to a red heat. As the carbon dioxide formed will be absorbed by the potassium hydroxide in the pipette, the reduction in volume gives the volume of the methane directly.

As the air enclosed in the tube takes part in the combustion of the hydrogen, a correction is necessary for the oxygen thus removed; this is determined once for all, so that the necessary small correction, which may amount to about 0.8 c.c., can be applied in all the estimations.

The combustion with copper oxide has the great advantage over other methods that the whole of the gas left after absorption can be

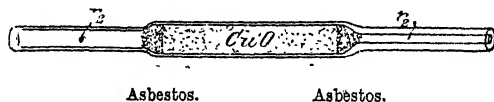


FIG. 94.

taken for the determination, so that any errors do not influence the final result to the same extent as when only a fraction of the residue is used. A disadvantage arises from the difficulty in completely burning the methane and from the high temperatures necessary for the combustion, as the tube must be allowed to cool down before reading off the volume; the copper oxide tube must also be reoxidised after each analysis. Further details are given under the description of Jaeger's method of gas analysis (p. 657). Jaeger's method, however, is frequently employed for the determination of the percentage of nitrogen only in gases; the percentage of nitrogen obtained in this way is more accurate than that found by the explosion method, in which it is always taken by difference, and is, therefore, subject to the combined errors in the determination of all the other constituents.

#### D. MODE OF PROCEDURE IN GAS-VOLUMETRIC ANALYSIS

It is customary to distinguish between "exact" and "technical" gas analysis in respect to the method of working adopted. In the former, mercury is usually employed as the confining liquid, and the smallest possible quantities of liquid are used for the absorption of the gases, so as to avoid the simultaneous absorption of other gases which are dissolved to a slight extent in aqueous solutions; also, the pressure and temperature are taken for each reading, and the gas volume corrected

to normal conditions. The normal volume is the volume which the dry gas occupies at 760 mm. mercury pressure and 0° C. If the observed gas volume be denoted by  $V$ , the temperature by  $t$ , the barometric pressure by  $b$ , and the pressure of aqueous vapour at  $t^\circ$  by  $s$ , then, according to the laws of Gay-Lussac and Boyle, the normal volume :—

$$V = V_1 \frac{273}{273+t} \times \frac{b-s}{760}$$

In technical gasworks analysis where the test is made by the litre or cubic metre, the correction is usually not made to normal volume, but to the volume of the gas, saturated with moisture, at 60° F. and 30 in. pressure (= 15° C. and 760 mm.; see p. 625).

The gas reduction Tables VI. and VII., given in the Appendix to Vol. I., can also of course be used for making the necessary corrections for the volume of dry gas at 0° C. and 760 mm. A table is given on p. 690 to facilitate the correction to the volume of moist gas at 60° F. and 30 in. pressure.

A very convenient and useful "gas-calculator" for the correction of the volumes of gases to normal temperature and pressure has recently been devised by R. C. Farmer.<sup>1</sup>

In technical gas analysis, water, or occasionally aqueous solutions, are used as the confining liquid, and no correction is made for the solubility of the gases concerned. According to Bunsen, the solubility of the following gases in 1 volume of water at 15° is :—

Nitrogen . . .	0.015	Carbon dioxide . .	1.032
Hydrogen . . .	0.019	Carbon monoxide . .	0.025
Oxygen . . .	0.030	Methane . . .	0.039
Ethylene . . .	0.162		

More recent determinations by L. W. Winkler give the values for oxygen and nitrogen at 16° as 0.033 and 0.016 respectively.

The extent of the absorption of gases by the confining liquid corresponds to the partial pressures of the several ingredients; with air, for instance, the absorption coefficient is 0.018. The error introduced by the absorption is sometimes compensated by previously saturating both the confining liquid and the absorption reagents with the gas to be analysed or with gas of similar composition.

A further inaccuracy in technical gas analysis may arise from variations in pressure and temperature that may occur during the course of the analysis and which are not fully corrected. Variations in pressure are hardly ever likely to occur during the period of an analysis; a change in pressure of 1 mm. corresponds to a change in volume of

<sup>1</sup> *Analyst*, 1910, 35, 308. The "gas-calculator" is supplied by Messrs Baird & Tatlock, Hatton Garden, London, E.C.

0.1 per cent. A change in temperature of  $1^{\circ}$  corresponds to a change in volume of 0.3 per cent.; it is, therefore, essential that the temperature of the room in which the analysis is conducted should be kept as uniform as possible; a northerly aspect for the room is always preferable. The most effective means of minimising changes in temperature is to provide the measuring tube of the apparatus with a water-jacket, and if possible to run a current of water of constant temperature through the jacket during the test. In the more accurate forms of apparatus in which mercury is used as the confining liquid, a compensating or "correction" tube is attached to the measuring tube by means of which the gas-volumes are corrected to normal temperature and pressure; this arrangement is described in connection with Sodeau's apparatus (Vol. I, p. 219). A "correction" tube can also be attached to the Hempel burette, but it is not commonly employed.

### 3. APPARATUS FOR GAS ANALYSIS

Of the many forms of apparatus for gas analysis that have been devised, those of Bunte, Orsat, Hempel, Sodeau, and F. Fischer have been described in the section on Technical Gas Analysis, in Vol. I.; the last three of these are applicable to the complete analysis of coal gas. The adaptation of the Bunte burette for this purpose is fully described in the German edition,<sup>1</sup> in which an account is also included of Drehschmidt's apparatus<sup>2</sup> for gas analysis; neither of these forms of apparatus are in general use in this country for the complete analysis of coal gas. The apparatus devised respectively by Pfeiffer, Bone and Wheeler, and Jaeger, the last especially in reference to the estimation of nitrogen, are described below, as these have not been included in the section on Technical Gas Analysis in Vol. I.

#### 1. Pfeiffer's Apparatus.<sup>3</sup>

The following considerations have been put forward by Pfeiffer in regard to the method of analysis adopted with his apparatus.

Since the errors that may arise in the estimation of carbon monoxide by absorption with cuprous chloride are not altogether overcome by using a second absorption pipette, as a partial absorption of the residual gases, other than carbon monoxide, may possibly occur, Pfeiffer is of opinion that it is both simpler and more accurate to estimate the carbon monoxide by explosion, simultaneously with the determination of the hydrogen and methane. From his experience he regards it also as preferable to oxidise the hydrogen and methane together, rather than to adopt the method of fractional combustion. From these considerations the course of analysis adopted consists in the successive estimation of the carbon dioxide, heavy hydrocarbons, oxygen, and

<sup>1</sup> Vol. III., pp. 254-261.

<sup>2</sup> *Ibid.*, pp. 264-266.

<sup>3</sup> *J. Gasbeleucht.*, 1899, 42, 209.

possibly the hydrocarbon vapours by absorption, and the combustion of the residual carbon monoxide, hydrogen, and methane. By estimating the carbon dioxide formed, the total contraction, and the residual nitrogen, after the removal of the excess of oxygen by means of phosphorus, the necessary data for calculation on the lines described on p. 638 are obtained. A complete analysis of coal gas can be carried out by this method in three-quarters of an hour, and very accurate results, it is stated, can be obtained.

The apparatus<sup>1</sup> consists of the burette and levelling flask (Fig. 95), two or three absorption pipettes (Fig. 90, p. 633), a phosphorus pipette, and an explosion pipette (Fig. 91, p. 642).

The burette B, which serves as the measuring tube, is provided with a stopcock *b*, and funnel, and is attached to the pipette P, as shown; the capacity of the burette is 100 c.c. The lower end of the burette is connected by the rubber tubing S, with the levelling bottle N, of 300 c.c. capacity. Water acidified with 0.5 per cent. of sulphuric acid is used in the confining liquid; this addition is to prevent the absorption of carbon dioxide and to take up ammonia vapour after the absorption of the hydrocarbon vapours.

To take the sample of the gas, the burette B is first filled completely with water by raising the levelling vessel and opening the stopcocks *b*<sub>1</sub> and *b* and the sample then drawn in by lowering the levelling bottle in the usual manner, until the volume of gas is a little below the zero mark; the stopcocks are then closed, and the levelling bottle again raised. To measure off exactly 100 c.c., the lower stopcock is carefully opened and the water allowed to rise to the true zero; the upper stopcock is then momentarily opened, and the volume checked in the usual manner with the levelling bottle N. In the first reading the zero lies as much below the zero mark as is equivalent to the content of the capillary at *b*, since the latter is filled with water in the subsequent measurements and the 100 c.c. graduation is at the lower end of the capillary. This correction (generally 0.2 c.c.) is, therefore, determined once for all as follows:—Air is introduced into the burette to about the division 90, then water until the capillary at *b* is filled, the stopcocks closed, and the reading taken after two minutes; meanwhile the water

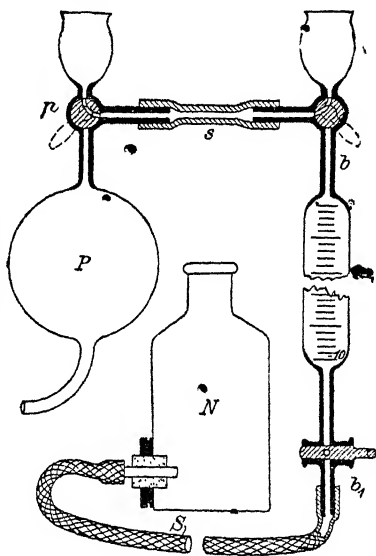


FIG. 95.

<sup>1</sup> The complete apparatus is made and supplied by H. Hürold, Glassblower, Magdeburg.

is completely removed from the capillary tube of the stopcock, the water then run out of the capillary into the burette and another reading taken; the difference between the two readings gives the capacity of the capillary. It is advantageous to use a meniscus screen, such as that of Göckel (Vol. I., p. 49), in taking the readings, so as to avoid parallax.

An improved form of burette designed by Pfeiffer,<sup>1</sup> especially for the analysis of coal gas, is shown in Fig. 96, and as arranged for the explosion of the combustible gases in Fig. 97. The bulb at the top of the burette is connected by a narrow tube to the lower bulb, which latter is provided with a mark *m*, which serves for measuring off the

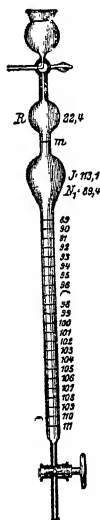


FIG. 96.

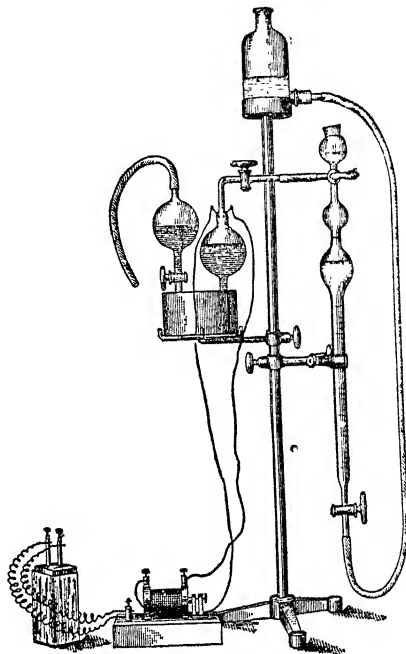


FIG. 97.

gas residue taken for combustion. The total capacity of the pipette between the two stopcocks is sufficient to contain the volume of air requisite for the combustion of the above gas residue. The relative capacities of the two spaces, for coal gas and for carburetted water gas, should be about 1 : 5. The capacity of the burette to *m* is marked (*R*), also the total capacity, *J*, and the volume of nitrogen contained in *J* when filled with air, *N*<sub>1</sub>.

*Carbon dioxide.* The pipette (Fig. 90, p. 633) is filled up to the tap with potassium hydroxide, and is connected with the burette as shown in Fig. 95. The stopcocks of both the burette and pipette are turned

<sup>1</sup> *Z. angew. Chem.*, 1907, 20, 22.

to the position in which the two funnels communicate with each other, water poured into one of them to expel the air from the connection *b-s-p*, the stopcocks of the pipette and of the burette turned through  $180^\circ$ , and the gas transferred from the burette into the pipette. While it is passing over, the contents of the pipette are shaken for a moment, so as to mix the water from the capillary connections with the alkali. As soon as the water reaches the stopcock *p*, the burette stopcock *b* is closed; the absorption is complete in one minute. The gas is then syphoned back to the burette by lowering the levelling bottle until the alkali reaches the stopcock *p* of the pipette, which is then turned through  $180^\circ$ , and the gas in the capillary, *p-s-b*, washed out as before by means of the water in the pipette funnel. The burette stopcock *b* is then closed and the reading taken as usual, after allowing to stand for one minute.

*Benzene vapour*.—This is absorbed with ammoniacal nickel cyanide solution (*cf.* p. 635); after shaking for three minutes (it is preferable to facilitate the shaking in this case by detaching the pipette), the residual gas is returned again to the burette where the absorption of the ammonia vapours is effected by the acidulated water used as the confining liquid. As a check, about 0.5 c.c. of fresh acidulated water is introduced into the burette from the pipette funnel.

*Total Heavy Hydrocarbons*, or only ethylene if benzene is previously absorbed, are determined by absorption with bromine water, and the bromine vapours subsequently removed by potassium hydroxide; three minutes, with frequent shaking, are necessary for the absorption.

*Oxygen* is estimated in the phosphorus pipette. The capillary space between the pipette and burette is cleared by forcing the water from the pipette into the burette funnel by attaching a piece of rubber tubing to the open end of the pipette and blowing.

*Carbon Monoxide, Hydrogen, Methane, and Nitrogen*. The explosion pipette (Fig. 91, p. 642) is used for the estimation of these gases. In the analysis of coal gas from 20 to 22 c.c. of the gas left after absorption, which requires about five volumes of air for combustion, are first measured off in the burette by allowing the excess to escape; since, in doing so, the capillary at *b* is freed from water, its capacity, as determined, must be added to the reading. The burette and explosion pipette are then connected, the air in the connecting capillaries displaced as in the case of the phosphorus pipette, and the gas passed over. The explosion pipette is then disconnected and the burette filled with air. The air is then transferred to the explosion pipette (Fig. 91), the water allowed to rise as far as the bulb of the pipette, the stopcock *a* then closed, and the small quantity of water remaining in the explosion chamber A withdrawn into the reservoir B, so that only the V-shaped connection remains filled with water; the stopcock *b* is then closed. An electric spark is then passed through the mixture in the usual manner,



the pipette stopcock carefully opened so that the enclosed water comes back into the explosion chamber quietly, and the residual gas, consisting of nitrogen, carbon dioxide, and a little oxygen passed back into the burette.

The carbon dioxide formed in the combustion is then absorbed with potassium hydroxide, and the excess of oxygen with phosphorus, whereby a direct measurement of the total nitrogen, inclusive of that added as air, is obtained.

*Calculation.* The gas residue after absorption admits of the following calculations:—

$$\begin{aligned} \text{H} &= \text{V} - \text{CO}_2 \\ \text{CO} &= \text{CO}_2 + \text{V} - \frac{2}{3}\text{C} \\ \text{CH}_4 &= \frac{2}{3}\text{C} - \text{V} \end{aligned}$$

The sequence of the separate readings and the resulting data are shown in the following analysis:—

Readings.	Data.	In Residue R.	In 100 parts of Gas.
<i>A. Absorption.</i>			
Initial reading . . . . .	100.0	...	...
After absorption with Alkali . . . . .	98.3	...	CO <sub>2</sub> = 1.70
After absorption with Nickel solution . . . . .	97.27	...	C <sub>6</sub> H <sub>6</sub> = 1.03
After absorption with Bromine . . . . .	94.48	...	C <sub>2</sub> H <sub>4</sub> = 2.79
After absorption with Phosphorus . . . . .	93.7	...	O = 0.78
<i>B. Explosion.</i>			
Gas residue taken (R) . . . . .	22.4	V = 21.55	H = 13.75
Air added (J) . . . . .	113.1	...	CH <sub>4</sub> = 6.05
Reading after explosion . . . . .	101.9	C = 41.40	CO = 1.75
Reading after absorption with Alkali . . . . .	94.1	CO <sub>2</sub> = 7.80	...
Reading after absorption with Phosphorus . . . . .	90.25	N <sub>1</sub> = 89.40	N = 0.85
			N = 3.56

## 2. Bone and Wheeler's Apparatus.

This apparatus,<sup>1</sup> which is exceedingly convenient for the rapid analysis of all gases met with in gasworks, is a simplified form of the apparatus employed by Bone for research purposes,<sup>2</sup> which was in turn a modification of the Frankland apparatus, including alterations introduced by Macleod and Dixon.

The general character and arrangement of the various parts of the apparatus is shown in Fig. 98. It comprises, essentially, three parts, viz.:—(1) a water-jacketed combination of measuring and pressure tubes, A and B, communicating, through the glass tap, C, with the mercury reservoir, D; (2) an absorption vessel, F, standing over mercury in a mahogany trough, G; (3) an explosion tube, E, fitted with firing wires, and connected with a separate mercury reservoir, H. All the connec-

<sup>1</sup> *J. Soc. Chem. Ind.*, 1898, 27, 10.

<sup>2</sup> *Proc. Chem. Soc.*, 1898, p. 154.

tions between A, E, and F are of capillary bore throughout, with suitable glass taps wherever necessary. The diagram also shows how connection is made between the measuring tube, A, and the special "sampling tube," K, whenever the latter is employed for the introduction

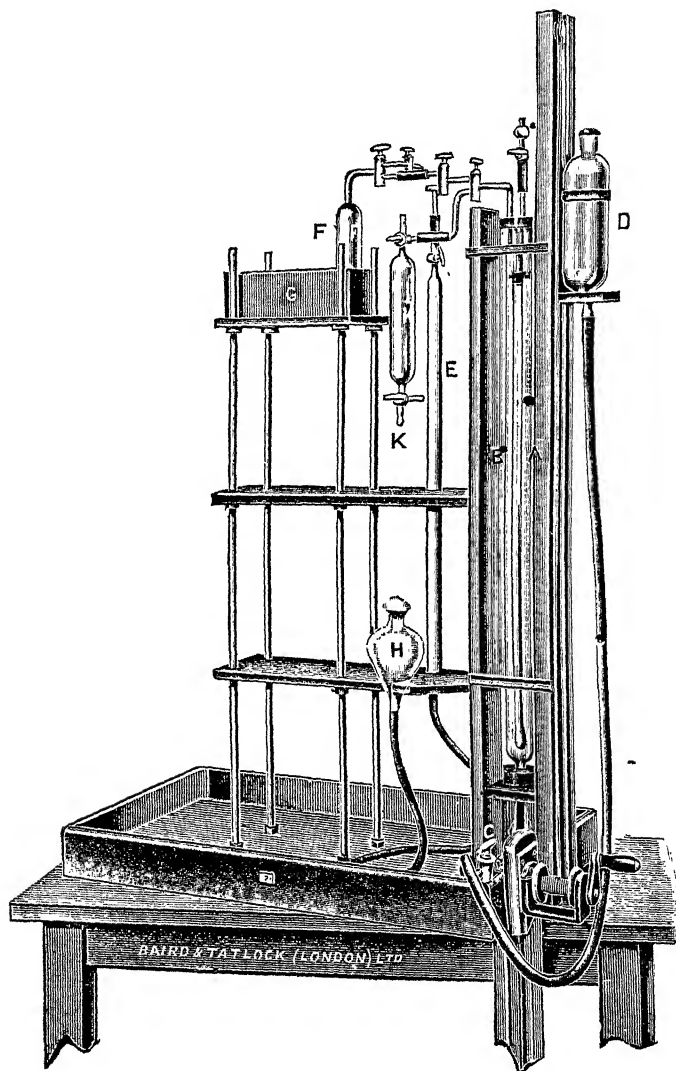


FIG. 98.

of the sample under examination. The sample may also be introduced into the apparatus, from an ordinary test tube, under the wide, open end of the absorption vessel, F, which has been previously filled with mercury. Before commencing an analysis, the whole of the apparatus, including all the connections between A, E, and F is completely filled

with mercury, and all the subsequent operations are conducted over mercury.

The various parts of the apparatus are suitably mounted on a strong wooden stand (oak or teak), with four vertical steel rods supporting the shelf upon which the mercury trough, G, rests; the same rods also carrying another shelf for reagent bottles. Proper provision is made for the raising or lowering (to the ground level, if required) of the mercury reservoir, D, by means of a wooden carrier with suitable pulley and ratchet wheel. The whole apparatus stands in a wooden tray 2 ft. 4 in. by 1 ft. 6 in. with 1 in. raised sides.

The salient features of the working of the apparatus are as follows:—

(1) The principle of measurement employed is that first introduced into gas analysis by Regnault, and subsequently adopted by Frankland, viz., the measurement of the pressure of the gas (in mm. of mercury) at constant volume. For this purpose the gas is brought to a certain "constant volume" mark in the measuring tube, A (by suitable manipulation of the mercury reservoir D and the tap C), and its pressure read off on the pressure tube, B. There are a series of such "constant volume" marks on A, each coinciding with a 100 mm. mark on the pressure tube, B (*i.e.*, with 0, 100, 200, etc., mm.), so that the actual pressure of the gas is given by subtracting from the "pressure reading" the numbers 0, 100, or 200, etc., according to the particular constant volume mark selected for the analysis. The tubes A and B are made in one piece, which is surrounded by a water jacket, and their inner surfaces are kept moist with very dilute sulphuric acid (1 in 20) as a precaution against the accidental fouling of the measuring tube with alkalis; the wetting of A and B with the same liquid eliminates the influence of water vapour upon the gas measurements, the various pressures representing those of the dry gas under examination. The tap closing the upper end of the pressure tube is connected with it by means of stout rubber pressure tubing, a device which gives a perfectly tight joint with sufficient elasticity to prevent fracture in case the mercury in B is inadvertently allowed to run up the tube with unusual velocity. This tap also allows of the vacuum being easily made in B whenever necessary. The advantages of this mode of measurement over the more usual method of determining the volume under atmospheric pressure are twofold, viz., (1) it allows of the use of smaller volumes of gas for an analysis, thus from 5 to 10 c.c. of gas can be made to have a pressure of 100 mm., according to the particular volume mark selected, and this pressure can easily be read off to within 0.2 mm. without employing a telescope; and (2) the measurements are, of course, independent of the barometric pressure, and at the same time are unaffected by the tension of aqueous vapour.

(2) The length of the pressure tube, B (about 700 mm.), amply pro-

vides for the proper dilution of the "explosive mixture" in an explosion analysis, even in the case of a rich gas such as coal gas.

(3) The arrangements for the various "absorptions" are of the simplest character, all being carried out over mercury in the one absorption vessel, F, in each case with a comparatively small volume of the particular reagent, which is always used fresh and is at once discarded after use.

To facilitate the introduction of the various reagents, and the rinsing out of the absorption vessel with water or dilute sulphuric acid *in situ* between each successive reagent, the wide (open) end of the vessel is immersed under the mercury in the trough, G, whilst the top terminates in a capillary three-way tap. One of the parallel branches of this tap communicates through a stout rubber joint, with the measuring vessel, A, and the other with a water pump, a large bottle being inserted between the pump and the absorption vessel to serve as a trap for either the mercury or the reagent which is being discarded after use. The insertion of a tap between the pump and the bottle obviates the necessity of the continuous exhaustion of the latter, a single exhaustion at the outset of an analysis being all that is required.

From 2 to 5 c.c. of the reagent to be used is introduced into the absorption vessel (previously filled with mercury), by means of a suitable pipette, from below the surface of the mercury in the trough. Any minute bubble of air accidentally introduced with the reagent can be got rid of by cautiously opening the branch of the tap leading to the above-mentioned exhausted bottle; the same device allows of the complete withdrawal of the reagent after use, without taking down the absorption vessel, and also of the rinsing out of the latter *in situ* with water, or dilute sulphuric acid, before the next reagent is used.

The apparatus is arranged for fixing at the right-hand end of the laboratory bench, the guide rail for the mercury reservoir D being extended to the ground level. A water supply and suitable waste pipe are required for the circulation of water through the water jacket surrounding the measuring and pressure tubes, and a filter pump for evacuating the large bottle used as a trap for the waste reagents and for any mercury carried over with them.

As the gas during the analysis is for the most part under considerably less than atmospheric pressure, it is essential for accuracy that the stopcocks should be perfectly tight; provided that care is exercised in their selection, and that they are carefully lubricated, no difficulty is experienced in this respect. A suitable lubricant is prepared by heating a mixture one part of vaseline and one-tenth to one-fifth part of paraffin wax on the sand-bath, and adding soft rubber clippings (preferably of unvulcanised rubber), stirring well till all the rubber is dissolved. The amount of rubber required varies considerably according to the quality used, and fresh quantities should be added until the mixture, on cool-

ing, has attained the desired consistency. In cleaning the stopcocks a soft linen rag should be used, to avoid any abrasion of the ground surfaces. After each analysis the apparatus should be washed out with 5 per cent. sulphuric acid.

In the analysis of illuminating gas, the sequence of operations is similar to that adopted with other forms of apparatus. The carbon dioxide is best absorbed with 25 per cent. potassium hydroxide solution, and the heavy hydrocarbons with a solution of bromine in aqueous potassium bromide, followed by potassium hydroxide. For the absorption of oxygen, 5 to 8 c.c. of very concentrated potassium hydroxide solution are first placed in the absorption vessel, and then 2 c.c. of pyrogallol solution (1 oz. in 100 c.c.). For the carbon monoxide, two absorptions with 8 to 10 c.c. of the solution of ammoniacal cuprous chloride, made up as described on p. 637, are made, and the gas washed with 5 per cent. sulphuric acid.

The whole of the residue is mixed with at least twice its own volume of excess oxygen or air, the quantity of gas originally taken being regulated to allow of this being done. The gas is transferred to the explosion tube, fired in the usual manner, under reduced pressure, then drawn back into the measuring vessel, and the contraction determined. The carbon dioxide formed by the explosion of the methane is then determined by absorption with potassium hydroxide.

The following table shows the method of recording the results in the case of an analysis of coal gas :—

- V = Constant volume mark selected on measuring tube.  
 R = Reading of barometer tube when gas is brought to the constant volume mark selected. Hence,  $R - V$  = pressure of gas.  
 T = Temperature of water jacket.  
 C = Contraction on explosion.  
 A = Absorption by potassium hydroxide after explosion.

	Constant Mark, V.	T.	R.	Difference.	Remarks.
Original gas . .	0	15°·2	168·0	...	Gas taken = 168·0.
After KOH . .	0	15°·2	164·0	4·0	$\text{CO}_2 = 4·0 \times 100 \div 168·0$ = 2·4 per cent.
„ Br . .	0	15°·2	158·1	5·9	$\text{C}_n\text{H}_m = 5·9 \times 100 \div 168·0$ = 3·5 per cent.
„ Pyrogallol . .	0	15°·2	157·6	0·5	$\text{O} = 0·5 \times 100 \div 168·0$ = 0·3 per cent.
„ $\text{Cu}_2\text{Cl}_2$ . .	0	15°·2	143·3	14·3	$\text{CO} = 14·3 \times 100 \div 168·0$ = 8·5 per cent.
Oxygen added . .	0	15°·2	588·1	...	$\text{CH}_4 = 52·9 \times 100 \div 168·0$ = 31·5 per cent. $\text{H} = \frac{2}{3}(228·6 - 2 \times 52·9) \times 100$ $\div 168·0 = 48·7$ per cent.
After explosion . .	0	15°·2	359·5	228·6C	
„ KOH . .	0	15°·2	306·6	52·9A	

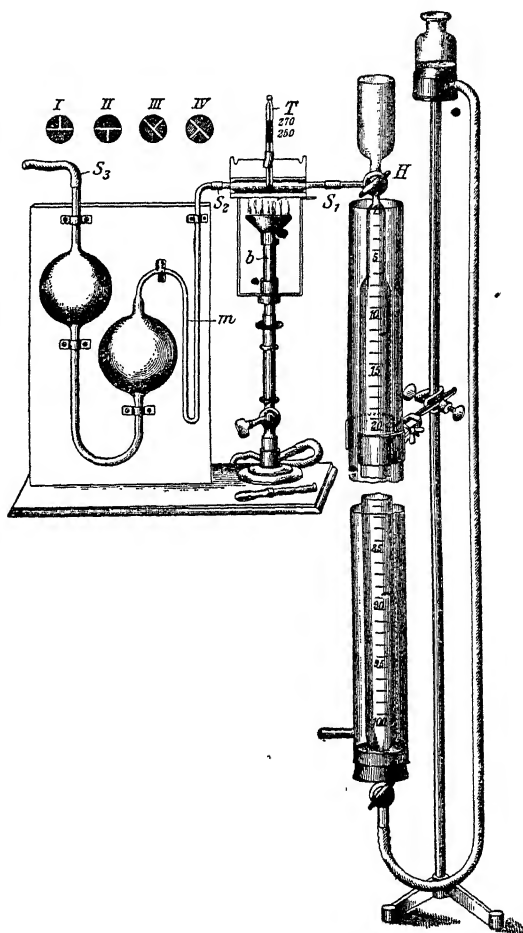
Therefore :—

$\text{CO}_2$	= 2.4 per cent.	$\text{CO}$	= 8.5 per cent.
$\text{C}_n\text{H}_m$	= 3.5 "	$\text{CH}_4$	= 31.5 "
$\text{O}_2$	= 0.3 "	$\text{H}_2$	= 48.7 "
$\text{N (by difference)} = 5.1 \text{ per cent.}$			

### 3. Jaeger's Apparatus.

The method of analysis adopted by Jaeger<sup>1</sup> consists in the estimation of carbon dioxide, heavy hydrocarbons, and carbon monoxide by absorption, followed by the fractional combustion of hydrogen and methane over copper oxide at different temperatures; no air is added for the combustion, so that the whole of the residual gas after the absorptions can be used for the estimation of these constituents. A further advantage of the method is that the nitrogen can be determined directly.

The apparatus employed is shown in Fig. 99. The burette is a modified form of that of Bunte, narrowed at the top to permit of more accurate readings and provided with a side exit tube; it is enclosed in a water jacket. The absorptions are carried out with pipettes, such as those of Hempel, on the usual lines. For the fractional combustion of the



• FIG. 99.

hydrogen and methane, the copper oxide tube (Fig. 94, p. 646) is connected up with short pieces of rubber tubing,  $s_1$ ,  $s_2$ , bound with wire, to a Hempel pipette filled with potassium hydroxide solution on

<sup>1</sup> *J. Gasbeleucht.*, 1898, 41, 264; *Z. angew. Chem.*, 1899, 12, 173.

the one side, and with the side tube of the burette on the other. Below the combustion tube is placed the Bunsen burner *b*, which is provided with a special regulating tap and a fan-shaped fitting to the burner. A framework of sheet iron attached to the burner carries a cover in which a short thermometer graduated up to  $270^{\circ}$  is fixed so that its bulb lies close to the side of the combustion tube. At the beginning of the test the solution in the pipette is forced up to the mark *m* of the capillary by blowing through the tube *s*, when the upper burette cock is in position I.; the stopcock is then closed with a quarter turn (position III.), and the tube slowly heated to  $250^{\circ}$  and kept at this temperature with as little variation as possible. As soon as this temperature is reached the upper stopcock of the burette is opened (position II.), then the lower one, and the levelling bottle raised. By passing the gas slowly from the burette to the pipette and back again the hydrogen is completely oxidised. After allowing to cool, the water in the pipette is again brought to the mark *m* and the residual gas measured.

A correction has to be applied for the oxygen of the air initially enclosed in the combustion tube, and which participates in the oxidation of the hydrogen. This is made, once for all, by filling the burette with pure hydrogen and determining the value of the correction; it amounts to approximately 0.5 c.c. and is to be subtracted from the hydrogen contraction found. The correction must also be taken into account in the determination of nitrogen at the end of the analysis.

For the subsequent combustion of the methane, the cover with thermometer over the combustion tube is removed, the tube heated with a more powerful flame to a bright red heat, and the gas repeatedly passed over the copper oxide till no further decrease in volume takes place. The carbon dioxide formed by the combustion is retained in the alkali pipette; the decrease in volume, therefore, corresponds directly (without correction) to the methane present. The residual gas must be allowed to cool completely to the temperature of the room before taking the final reading.

The incombustible gas residue, increased by the volume of the oxygen previously enclosed in the copper oxide tube and afterwards consumed (correction value), gives the nitrogen content of the gas.

For the determination of the percentage of nitrogen only in a sample of gas, the latter is placed in the burette, the copper oxide tube at once heated to a high temperature, and the gas passed backwards and forwards into the potash pipette until no further contraction occurs. The whole of the gaseous constituents, other than nitrogen, are thus completely removed, and the residual volume of gas, read after complete cooling, plus the previously ascertained correction for the oxygen content of the copper oxide tube, gives directly the amount

of nitrogen in the gas, and its percentage if 100 c.c. have been taken. Where many such tests have to be made, it is convenient to displace the air in the copper oxide tube by nitrogen previous to the test, in which case no correction is necessary.

After each test the copper oxide tube must be heated in a current of air to reoxidise the reduced copper.

The results obtained by this method are satisfactory as regards accuracy. The combustion of the methane is, however, very slow, and varies greatly according to the physical condition of the oxide of copper.

#### E. SPECIAL METHODS OF ESTIMATION OF CERTAIN CONSTITUENTS IN CRUDE AND PURIFIED ILLUMINATING GAS

Certain of the constituent gases and vapours present in illuminating gas cannot be readily estimated by the methods of volumetric gas analysis described above. In some cases, such as that of ethylene, this arises from the fact that no specific absorbent is known apart from those for other heavy hydrocarbons, whilst in the case of others, such as carbon bisulphide and naphthalene, the quantity present is too small to be estimated by the diminution in volume effected by direct absorption. In such cases special gravimetric, volumetric, or colorimetric methods are employed.

In general, the same methods may, with slight modifications, be employed both in testing the crude and purified gas, the amount of reagent employed and quantity of gas passed in the test being varied according to the amount of the particular constituent which is expected to be present.

In making tests with crude gas, certain precautions must be taken if results of any reasonable degree of accuracy are to be obtained. The interior surface of the mains of the manufacturing plant is usually coated with tar and ammoniacal liquor or water, and if gas be taken for such tests from a cock on the main, or from a small service pipe leading from the main, the slow stream of gas employed in making the test is largely drawn from that travelling along the surface of the main, which, by the action of the tar and liquor on that surface, is often materially altered in composition as compared with the bulk of the gas passing through the main at that point, with the result that incorrect and often very misleading results are obtained. The most satisfactory plan is to place a cork carrying a piece of glass tubing into a suitable hole bored in the main and closed by a plug when not in use, the end of the glass tube projecting well into the main. The other end of this tube is coupled, with as short connections as possible, to the absorbing apparatus, rubber connections being avoided as far as practicable; and where connections have to be made with such tubing, the ends of the glass



tubes joined should be brought close together within the rubber tube, so as to expose a minimum of rubber surface to the gas.

Where a direct connection to the main cannot be made in this manner, and a service pipe leading from it must be utilised, arrangements must be made to ensure the passing of a rapid stream of gas through the latter whilst the test is in progress, the gas actually used in this test being taken off from this service by means of a suitable T-piece. These precautions are also advisable even when testing purified gas, although the error caused by their non-observance is usually not so great.

The constituents, for which special methods of estimation are described, are as follows:—(1) Ethylene, (2) Benzene vapour, (3) Acetylene, (4) Oxygen, (5) Carbon dioxide, (6) Carbon monoxide, (7) Sulphuretted hydrogen, (8) Carbon bisulphide, (9) Total Sulphur compounds other than sulphuretted hydrogen, (10) Ammonia, (11) Hydrocyanic acid, (12) Naphthalene, (13) Tar-fog.

### I. Ethylene.

As already mentioned, both benzene vapour and ethylene are completely removed from coal gas by the action of bromine, but whereas the latter combines with the bromine to form the stable compound, ethylene dibromide,  $C_2H_4Br_2$ , the benzene vapour appears to be mechanically removed as a mixture of bromine and benzene, or possibly as a very unstable additive compound, which yields up the whole of its bromine to any substance which reacts readily with bromine, such as potassium iodide. Haber and V. Oechelhäuser<sup>1</sup> have based a method for estimating ethylene, and indirectly benzene, in coal gas on this difference of behaviour.

About 90 c.c. of the gas are run into a Bunte burette, the confining water sucked out in the usual manner, and a standard solution of bromine water (about half saturated) allowed to run into the burette up to a definite mark, which is noted (*e.g.*, the 5 c.c. mark). A little water is then allowed to enter to clear the capillary tube and stopcock of bromine water, and the burette shaken for two minutes, after which the colour of bromine vapour should still be distinctly visible. After a further three minutes, a solution of potassium iodide is sucked into the burette, the latter washed out with water, and the iodine liberated by the unaltered bromine titrated with sodium thiosulphate and starch. A blank test of the bromine water is made by drawing up some of the solution to the same mark as before, adding potassium iodide, and titrating the solution with sodium thiosulphate and starch. The difference in the quantities of *N*/10 thiosulphate used in the two tests gives the amount of bromine which has combined chemically with the

<sup>1</sup> *J. Gasbeleucht.*, 1900, 43, 347.

ethylene; 1 c.c. of  $N/10$  thiosulphate corresponds to 1.2 c.c. of ethylene at  $15^\circ$  and 760 mm., or  $60^\circ$  F. and 30 in.

Homologues of ethylene, if present, also combine with bromine, but as unit volume of any olefine combines with the same quantity of bromine, the total volume of olefines is correctly given by the test. Unsaturated hydrocarbons of other series, such as acetylene and its homologues, interfere with the results, as these absorb a much larger amount of bromine. For coal gas the amount of such hydrocarbons is too small to have a material effect, but according to Fritzsche,<sup>1</sup> they are present in oil gas in considerable quantity, and the method is not applicable to such gases.

## 2. Benzene.

The method of volumetric estimation by means of ammoniacal nickel cyanide has been described (p. 635), but sufficient experience has not yet been gained with the process under varying conditions to judge of its reliability. When the ethylene has been determined by the method described above, and the total percentage of heavy hydrocarbons by absorption with bromine or fuming sulphuric acid, that of benzene is given by the difference between the two values.

Numerous other methods have been proposed, but none of them have been generally adopted, partly on account of their being only approximate, and partly on account of the complicated mode of procedure suggested. According to Pfeiffer, a fair approximation of the amounts of olefines and benzene hydrocarbons may be calculated from the specific gravity of the gas as determined by one of the methods described later. From this observed specific gravity and the percentages of the remaining constituents, the specific gravity of all of which are known, the average specific gravity of the heavy hydrocarbons may be calculated. As the average specific gravities of the olefines present in coal gas is about 1.0, and that of the benzene hydrocarbons about 1.8, then if the specific gravity of the heavy hydrocarbons thus found by calculation is  $s$ , the volume percentage of benzene is found by the equation:—

$$\text{Benzene per cent. by volume} = \frac{(s - 1) \times \text{per cent. } C_nH_m}{1.8}$$

The percentage of ethylene is found by difference.

St Claire Deville<sup>2</sup> determines the amount of benzene and its homologues by passing the dried gas through a glass cooling-coil surrounded by a mixture of ice and salt, thus cooling to  $-22^\circ$ ; the condensed hydrocarbons are collected in a tube and weighed. A correction is made for the amount of benzene still left in the gas at this temperature, which amounts to 23.5 g. of benzene per cubic metre (0.67 g. or 10.33 grains

<sup>1</sup> *J. Gasbeleucht.*, 1902, 45, 281.

<sup>2</sup> *Ibid.*, 1899, 42, 652.

per cubic foot). Harbeck and Lunge,<sup>1</sup> have described a method of determination by conversion into dinitrobenzene which has been much simplified by Pfeiffer.<sup>2</sup> The latter converts the benzene vapour into dinitrobenzene by treating about 500 c.c. of the gas, contained in a separating funnel, with sulphuric and nitric acids, and estimates the dinitrobenzene produced by titration with stannous chloride according to Limpricht's method.<sup>3</sup>

For most gasworks purposes, the determination of the amount of benzene is rarely required, but in coke-oven works where the gas made is frequently washed with tar oils to recover the vapours of benzene and its homologues, a knowledge of their amount is desirable. The method usually adopted is to pass from 40 to 100 cb. ft. of gas through a series of four bottles, each charged with about 150 c.c. of heavy tar oil, which has been previously distilled till the thermometer in the vapour reaches 270°. The gas is bubbled through the bottles at a rate not much exceeding 1 cb. ft. per hour, and when the required amount of gas has been passed, the combined oil from the flasks is distilled, using a 3-bulb Le Bel-Henninger fractionating column, the distillation being continued up to 140°, and the distillate collected in a measuring cylinder. This consists chiefly of benzene with smaller quantities of toluene and xylenes. The method is, of course, not a very exact one, but gives results which agree fairly closely with the yields actually obtained on the large scale in the extraction of the benzene hydrocarbons.

Vapours of higher boiling liquids in the gas may be estimated approximately in a similar manner. In this case about 100 cb. ft. are passed through a train of wash-bottles containing heavy oils previously freed from low-boiling constituents. The contents of these are then distilled till the thermometer reaches 270°, and the distillate then fractionated, using a 3-bulb Le Bel-Henninger column, and the volume of distillate for each 10° interval, up to 210°, measured.

### 3. Acetylene.

This hydrocarbon is only present in coal gas in small quantity, generally not exceeding 0.1 per cent. For its estimation, the gas, purified if necessary from sulphuretted hydrogen, is passed through two Volhard absorbing bottles, each charged with 20 c.c. of concentrated ammoniacal silver nitrate solution, which absorbs the acetylene with formation and precipitation of silver acetylide, some silver being also formed by the reducing action of other constituents of the gas. The filtered and washed precipitate is cautiously treated with dilute hydrochloric acid on the filter till acetylene ceases to come off, the resulting mixture of silver chloride and silver digested with ammonia,

<sup>1</sup> *Z. anorg. Chem.*, 1898, 16, 41.

<sup>2</sup> *J. Gasbeleucht.*, 1899, 42, 697; *Chem. Zeit.*, 1904, 28, 884.

<sup>3</sup> *Ber.*, 1878, 11, 35.

filtered, the precipitate washed with ammonia, and the combined filtrates treated with nitric acid to precipitate the silver chloride, which is filtered off, and weighed; 1 g. of silver chloride corresponds to 0.09072 g. or 84.03 c.c. of acetylene measured moist at 15° and 760 mm.

#### 4. Oxygen.

The technical importance of the determination of oxygen is more especially in connection with the purification of illuminating gas from sulphuretted hydrogen by means of oxide of iron, and also (where this is carried out) of carbon bisulphide by means of lime. In order that the oxide of iron used may be revived *in situ* the gas entering the purifiers should always contain some oxygen. The most suitable proportion depends somewhat upon local circumstances, but as a general rule, it is found that the average percentage of oxygen should be rather more than one-half the average percentage of the sulphuretted hydrogen. Where lime is used for the simultaneous removal of sulphuretted hydrogen, carbon dioxide, and carbon bisulphide, the quantity of oxygen present at the purifier inlet is of the utmost importance, as the proper removal of the bisulphide depends very largely upon this point, too large an excess of oxygen causing the oxidation of the calcium sulphides as fast as they are formed, and so preventing their absorption of carbon bisulphide, whilst in entire absence of oxygen, the sulphide formed is inactive. The most favourable proportion of oxygen is somewhat less than one-half the average amount of sulphuretted hydrogen; if the percentage of carbon dioxide in the crude gas is as high as 3 per cent., a rather smaller proportion is advisable.

For purification control purposes, the volumetric estimation of oxygen by means of phosphorus, after removal of the heavy hydrocarbons by bromine, when carried out with ordinary precautions, gives results of quite sufficient accuracy.

A colorimetric method of estimation has been devised by Pfeiffer,<sup>1</sup> depending on the depth of colour produced by a known volume of the gas in an alkaline solution of pyrogallol, this being compared with standards of iodine in potassium iodide solution made up to match the colours given by known percentages of oxygen. Lubberger<sup>2</sup> has applied Winkler's method for estimating dissolved oxygen in water (Vol. I., p. 782) to the estimation of oxygen in coal gas, the gas being shaken in a Bunte burette with alkali and manganous hydroxide in oxygen-free water, the manganese being oxidised to hydrated peroxide. The latter is then treated with potassium iodide and hydrochloric acid, which results in the liberation of iodine in equivalent amount to the oxygen taken up by the manganous hydroxide, the quantity of which is estimated by  $N/100$  sodium thiosulphate in the usual manner.

<sup>1</sup> *J. Gasbeleucht.*, 1897, 40, 354.

<sup>2</sup> *Ibid.*, 1898, 41, 695.

### 5. Carbon Dioxide.

The estimation of this constituent in illuminating gas by absorption with aqueous potassium hydroxide is not very accurate, owing to the fact, already mentioned, that this reagent also tends to absorb some of the hydrocarbon vapours present. When greater accuracy is required, gravimetric or volumetric methods are employed; the former are carried out by absorbing the carbon dioxide in a weighed tube of soda-lime, and the latter by treatment of the gas with standard baryta water by Pettenkofer's method. In the former method, the gas, if unpurified, must be first freed from ammonia by passing through dilute acid, and from tar-fog and sulphuretted hydrogen, by passing through a tower filled with hydrated ferric oxide. The gas is then led through the meter, dried by calcium chloride, and passed into the weighed soda-lime tube, the last part of which is charged with calcium chloride to prevent loss of moisture. Each gram of  $\text{CO}_2$  found equals 544 c.c. of the gas measured moist at  $15^\circ$  and 760 mm. \*



FIG. 100.

For the estimation by means of baryta water, a convenient method is to employ a bottle of about 2 litres capacity, having a doubly bored rubber cork fitted with a small separating funnel of about 50 c.c. capacity, and a right-angled delivery tube, as shown in Fig. 100. The exact capacity of the bottle is determined by weighing it empty and then filled with water, the delivery tube being removed, and the stem of the funnel filled with water up to the stopcock; the difference of weight in grams gives the volume in cubic centimetres. To fill the bottle with saturated gas, one or two drops of water are added, the apparatus inverted, and gas passed in through the separating funnel and out through the delivery tube; two to three minutes' passage of a moderate stream of gas suffices to drive out all air. The delivery tube is then removed, replaced by a glass plug, the separating funnel stopcock closed, and the gas shut off and disconnected. The stopcock is then again opened for a second to allow the gas in the bottle to attain atmospheric pressure, and the height of the barometer and the room temperature noted.

As soon as the gas in the funnel has been replaced by air, 50 c.c. of baryta water of known strength (20 g. barium hydroxide per litre), and a little phenolphthalein are run into the funnel, and thence, by careful opening of the cock, into the bottle, cooling under the tap, if necessary, to create a slight vacuum; the funnel is then washed out with water into the bottle, care being taken that the stem of the funnel is left full of water. The bottle is well shaken, and allowed to stand for ten minutes, when absorption is complete. The stopcock is then opened, the contents of the bottle, including the precipitate,

washed out into a flask, and titrated at once with  $N/10$  oxalic acid, using phenolphthalein as indicator. Fifty c.c. of the original baryta solution are titrated in the same manner; the difference between the quantity of oxalic acid solution required for neutralisation represents the amount of alkali corresponding to the carbon dioxide absorbed, expressed in decinormal solution; each cubic centimetre of  $N/10$  oxalic acid corresponds to 0.0022 g., or to 1.119 c.c. of dry  $\text{CO}_2$  at  $0^\circ$  and 760 mm. To obtain the percentage of the gas, the volume of  $\text{CO}_2$  under these conditions must be converted in the usual manner into the volume of moist gas measured at the same temperature and pressure as observed with the volume of gas taken. If  $n$  equals the number of cubic centimetres of  $N/10$  oxalic acid found,  $v$  the capacity of the bottle in cubic centimetres,  $t$  the temperature,  $s$  the vapour pressure of water at that temperature, and  $b$  the height of barometer, the percentage of  $\text{CO}_2$  is found by the equation:—

$$\begin{aligned}\text{Percentage of } \text{CO}_2 &= \frac{n \times 1.119 \times (273 + t) \times 760 \times 100}{273 \times (b - s) \times v} \\ &\quad \begin{array}{cc} \text{Constants.} & \text{Variants.} \end{array} \\ &= \frac{1.119 \times 760 \times 100}{273 \times v} \times \frac{n \times (273 + t)}{b - s}\end{aligned}$$

When  $v$  has been determined, a simple figure for the constants can be calculated once for all.

## 6. Carbon Monoxide.

For most gasworks purposes this is determined by the gas-volumetric method described (p. 636). For the estimation of small quantities, such as those caused by escape of waste gases, etc., into the air, more delicate methods are employed; these are fully described in the section on "Air" (Vol. I., p. 889).

## 7. Sulphuretted Hydrogen.

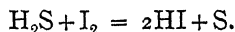
For the control of the purification process in gasworks, the estimation of sulphuretted hydrogen by volumetric absorption with a solution of cadmium sulphate or chloride gives results of sufficient accuracy. For more accurate determinations, especially when only small quantities are present, other methods must be employed. The gas tested must be freed from tar-fog and ammonia if present; the former is removed by a small cotton-wool filter, and the latter by washing with dilute sulphuric acid.

(i.) *Gravimetric Estimation.* For this purpose, Fresenius<sup>1</sup> employs as absorbent, pumice stone which has been treated with saturated copper sulphate solution, dried, and heated for four hours at  $250^\circ$ .

<sup>1</sup> *Quantitative Analysis*, 7th ed., vol. i., p. 383.

According to L. T. Wright,<sup>1</sup> the copper phosphate obtained by the precipitation of a copper sulphate solution with sodium hydrogen phosphate is a more suitable absorbent. To prepare it, a solution of 100 g. of crystallised sodium hydrogen phosphate in 500 c.c. of water is added, with constant stirring, to one of 125 g. of crystallised copper sulphate in 750 c.c. of water, the precipitated phosphate being filtered off and dried at 100°. Either reagent is placed in a U-tube so as to occupy about five-sixths of its length, the remaining one-sixth being filled with calcium chloride. The gas, freed from tar-fog and ammonia as described, is dried by calcium chloride, and passed through the weighed U-tube containing the copper sulphate or phosphate, and thence through a meter or into a graduated aspirator. At the end of the test, dry air is drawn through the U-tube, which is then weighed, the increase of weight giving the weight of H<sub>2</sub>S in the volume of gas passed. One gram of H<sub>2</sub>S equals 697.6 c.c. or 0.02464 cb. ft. of moist gas at 15°, and 760 mm.

(ii.) *Volumetric Estimation.* The most suitable reagent is a standard solution of iodine in potassium iodide, which reacts with sulphuretted hydrogen yielding sulphur and hydrochloric acid, according to the equation:—



This reaction may be carried out in a Bunte burette,<sup>2</sup> using a solution of iodine in potassium iodide containing 1.0526 g. of iodine per litre, 1 c.c. of which = 0.1 c.c. of H<sub>2</sub>S measured moist at 15° and 760 mm. The gas to be tested, after freeing from tar-fog and ammonia, is passed into the completely dry burette (if necessary with the assistance of an aspirator), and a portion of the gas then sucked out to make room for the reagents. The iodine solution is then sucked in from a small dish so as to fill the capillary and bore of the stopcock, and then starch solution to the lowest division mark (—10). By gradually adding fresh quantities of iodine, and repeated shaking, the end-point of the reaction is recognised by the formation of a permanent blue colour. The amount of iodine used is read off directly on the burette, the amount remaining in the capillary being balanced by that added before the starch, which is not measured. The volume of gas used is then determined in the usual manner.

An alternative method consists in employing a dry bottle of known capacity (about 500 c.c.) closed with a hollow stopper capable of holding 25 c.c. (A glass tube of this capacity, closed at one end and fitted into a rubber cork the bottom of which is coated with a film of paraffin wax, may be substituted for a ground-in stopper.) The gas, purified from tar-fog and ammonia, is blown through the inverted bottle till all

<sup>1</sup> *J. Soc. Chem. Ind.*, 1885, 4, 665.

<sup>2</sup> *Cf. Bunte, J. Gasbeleucht.*, 1888, 31, 899; Kast and Behrend, *Ibid.*, 1889, 32, 159.

air is driven out, the tube or stopper, to which 25 c.c. of  $N/10$  iodine solution has been added, inserted whilst the bottle is still inverted, and the solution shaken with the gas; the contents of the bottle and stopper are then washed out, and the excess of iodine determined by titration with sodium thiosulphate and starch. Each cubic centimetre of iodine solution used equals 1.122 c.c. of dry  $H_2S$  at  $0^\circ$  and 760 mm.; the percentage of the gas is calculated in exactly the same manner as that of carbon dioxide given on p. 665, with the substitution of the figure 1.108 for that of 1.119 in the equation.

The iodine method is likely to give high results, inasmuch as the unsaturated compounds and also hydrocyanic acid, when present in the gas, tend to combine with iodine. With coal gas the error thus caused is usually small, but it is very considerable in the case of oil gas and of carburetted water gas, owing to the presence of cyclopentadien,  $C_5H_6$ .<sup>1</sup>

C. W. Somerville<sup>2</sup> has recently described a modified iodometric method in which the gas is drawn, by means of an aspirator, through a wash-bottle of 100 c.c. capacity containing 10 c.c. of  $N/1000$  iodine solution and 10 c.c. of specially prepared starch solution diluted to 100 c.c. The passage of the gas is continued until the blue coloration just disappears, the volume of gas used being found from the volume of water run off from the aspirator. To obviate the error due to the above-mentioned impurities, a second test is made with the same gas, which is first passed through a small tower containing lead carbonate to remove sulphuretted hydrogen; by deducting the second result from the first the true amount of sulphuretted hydrogen is found.

(iii.) *Colorimetric Estimation.* The colorimetric method devised by Vernon Harcourt is very convenient for the estimation of sulphuretted hydrogen, especially where this impurity is only present in small quantity. In this process the gas is bubbled, in a fine stream, through a standard sized tube containing a solution of lead in excess of sodium hydroxide, to which sugar is added, the passage of the gas being continued until the solution attains the same brown colour as the similar sized standard tube (see Fig. 101, p. 669), which is artificially made to correspond with the colour given to the standard lead solution by 0.0025 grains (0.000162 g.) of sulphur, by mixing solutions of copper, cobalt, and ferric sulphates. The gas is drawn through the solution by an aspirator, which is completely filled with water at the commencement, the water run out being collected in a measuring cylinder, thus giving a direct reading of the volume of gas passed. This volume of gas, therefore, contains the above quantity of sulphur as sulphuretted hydrogen, and from this figure either the percentage, or amount in any given volume, is readily calculated.

<sup>1</sup> Cf. also Ross and Race, *J. Soc. Chem. Ind.*, 1910, 29, 604.

<sup>2</sup> *J. Gas Lighting*, 1910, 112, 29.

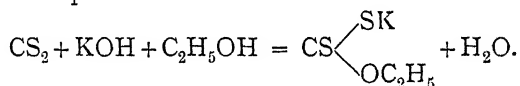


The brown solution becomes colourless on exposure to light, and provided that carbon dioxide is excluded the revived solution may be used over again for a considerable number of estimations.

### 8. Sulphur Compounds other than Sulphuretted Hydrogen ; Carbon Bisulphide.

Coal gas purified by means of oxide of iron, always contains small quantities of volatile sulphur compounds other than sulphuretted hydrogen. The vapour present in largest quantity is that of carbon bisulphide, the amount of which varies from 10 to 80 grains per 100 cb. ft., according to the variety of coal carbonised and the conditions of distillation. In addition, from 5 to 10 grains of sulphur is present in the form of other compounds, among which thiophene, carbonyl sulphide, and alkyl mercaptans, and sulphides have been detected.

For the estimation of carbon bisulphide, a measured volume of the gas freed from sulphuretted hydrogen, if necessary, by iron oxide, is dried by calcium chloride and passed through two wash-bottles containing a solution of potassium or sodium hydroxide in absolute alcohol, which converts the bisulphide into potassium or sodium xanthate according to the equation:—



The gas and reagent must be kept as free as possible from water, as small quantities of the latter greatly decrease the absorbing power of the reagent for the bisulphide. The quantity of xanthate or of sulphur in the solution obtained may then be ascertained by the methods given on p. 630, for the estimation of carbon bisulphide in commercial benzene.

The carbon bisulphide may also be estimated by Harcourt's colorimetric method. This depends on the fact that when coal gas containing carbon bisulphide is passed over platinised pumice, the latter is converted into sulphuretted hydrogen, which is then estimated colorimetrically in the manner described under sulphuretted hydrogen (p. 667). To carry out the test, a small fractionating flask of about 30 c.c. capacity filled with platinised pumice is placed in a special stand surrounded by a glass chimney (Fig. 101), so that the bottom of the flask is about 1 in. above the small ring burner fixed at the bottom of the chimney. The latter is lighted, turned down until the flame just shows a slight luminosity, and the gas then allowed to pass, at the rate of about 0.5 cb. ft. per hour, through the platinised pumice, which is thus heated to about 300° to 350° C.

After about ten minutes, the delivery tube is connected to the tube

containing the lead acetate syrup, and the latter to an aspirator, and the gas passed in a thin stream through the tube until it has reached the same depth of colour as that of the standard cylinder, corresponding to 0.0025 grain or 0.000162 g. of sulphur. The volume of gas containing this quantity of sulphur as carbon bisulphide is obtained from the amount of water run from the aspirator and collected in the measuring cylinder; from these data the amount of sulphur present in the gas as carbon bisulphide is readily calculated.

This method, whilst very rapid and convenient, only gives results of fair accuracy if the gas tested is free from oxygen, or only contains this gas in very small quantity. Mostly, however, the purified coal gas contains appreciable quantities of oxygen, which in presence of the hot

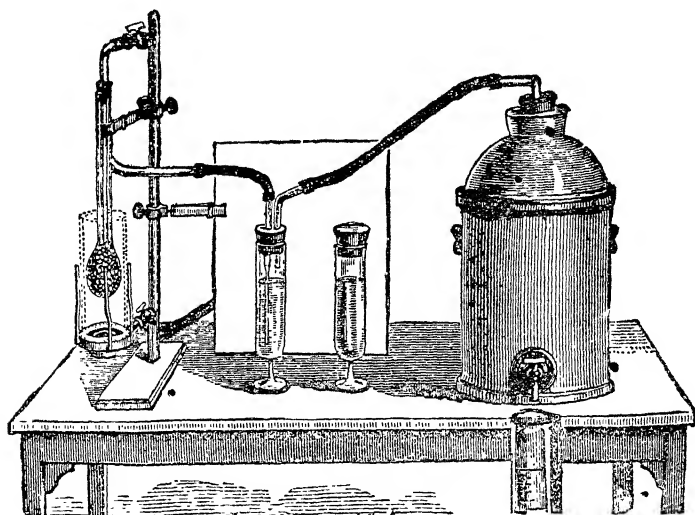


FIG. 101.

platinised pumice acts on the sulphuretted hydrogen produced, converting it into sulphur and water, the latter condensing in the delivery tube of the flask; the results then obtained are much below the true figure.

### 9. Total Sulphur.

In most instances, the separate determination of carbon bisulphide is not carried out, as all the information usually required is obtained by the estimation of the total sulphur present, by burning a known volume of gas and estimating the sulphur in the products of combustion.

In this country the method almost always employed is that used by the Metropolitan Gas Referees for testing London gas; it is generally known as the "Referees'" method. The gas is burnt in a small Bunsen burner with a steatite top (Fig. 102), which is mounted on a short

cylindrical stand, perforated with holes for the admission of air, and having on its upper surface, which is also perforated, a deep circular channel to receive the wide end of the trumpet tube. On the top of the stand are placed lumps of fresh, commercial sesquicarbonate of ammonia, weighing in all about 60 g. The upper, narrow horizontal

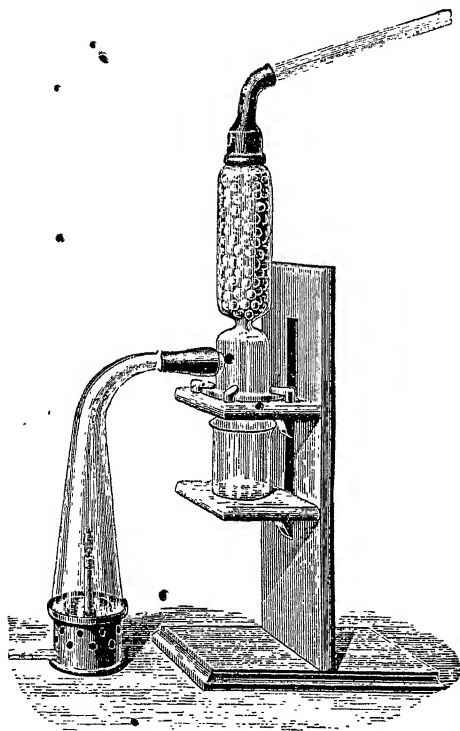


FIG. 102.

end of the trumpet tube is connected by flexible tubing with the side tubulure of a vertical glass cylinder, constricted above the tubulure to about half its diameter, the space from the contracted neck to the top being filled with glass balls about 15 mm. in diameter, to break up the current of gas and promote condensation. To the top of the condenser a long glass tube slightly bent over at the upper end is affixed by means of a cork or rubber tubing; this serves to effect further condensation as well to regulate the draught and afford an exit for the waste gases. At the bottom of the condenser is fixed a small glass tube drawn out to a jet, through which the liquid formed during the test drops into a flask beneath. The test should be

carried out in a room in which no other gas is burnt, and the air of which is not otherwise contaminated with sulphur dioxide.

The gas is burned at the rate of 0.5 to 0.7 cb. ft. per hour, the trumpet tube being placed on the burner when the meter index passes a point which is noted. The products of combustion, together with the ammonia evaporated from the carbonate, pass through the condenser, where the sulphur dioxide is condensed from the products as a solution of ammonium sulphate, the excess of oxygen present effecting the oxidation of the sulphite to sulphate. As soon as the required quantity of gas has been passed, the supply is shut off. For official purposes, meters are used which are arranged to cut off the gas supply automatically when 10 cb. ft. have passed, and to record the time at which this takes place. For unofficial tests this is, of course, unnecessary. After cooling, the condenser tube and cylinder are washed out with distilled

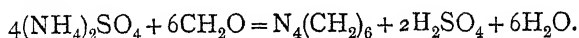
water into the beaker or flask containing the condensed liquid, and the sulphur in the latter determined in the usual way, either in the whole or in an aliquot part of the solution, by precipitation with barium chloride. From the weight of barium sulphate obtained, in grams, the sulphur in grains per 100 cb. ft. is readily obtained:—

$$\text{grs. per 100 cb. ft.} = \frac{\text{g. BaSO}_4 \times 15.432 \times 0.1374 \times 100}{\text{gas consumed corrected to } 60^\circ \text{ F. and } 30 \text{ in. Bar.}}$$

The correction of the gas volume to  $60^\circ \text{ F.}$  and 30 in. pressure is found by the table on p. 690.

The method tends to give results which are slightly low owing to incomplete oxidation of the sulphites to sulphates, the former not being precipitated with barium salts. To avoid this possibility, some analysts prefer to oxidise the solution with bromine water before precipitation, whilst others oxidise with nitric acid, and precipitate with barium nitrate instead of chloride. T. Fairley<sup>1</sup> dispenses with the use of ammonium carbonate, and allows a solution of hydrogen peroxide to drip down the condensing cylinder of the Referees' apparatus, the sulphur being then obtained in the condensate as free sulphuric acid. Instead of using the gravimetric method, the amount of sulphuric acid may be then determined by titration with normal alkali, provided that the hydrogen peroxide solution used is neutral. Or, by using a known volume of hydrogen peroxide solution of determined acidity, the sulphuric acid formed may be found by deducting the amount of the latter from the total quantity of acid found.

H. Blair<sup>2</sup> has proposed the following volumetric method for the estimation of the sulphuric acid in the solution obtained by the Referees' process. An aliquot portion of the solution is boiled to volatilise the ammonium carbonate, thus leaving neutral ammonium sulphate; an excess of neutral formaldehyde solution (about 30 per cent.) is then added to the hot solution, which combines with the ammonia, forming hexamethylene tetramine, and liberates sulphuric acid, in accordance with the equation:—



The liberated sulphuric acid is then determined by titration with  $N/10$  alkali, using phenolphthalein as indicator; 1 c.c.  $N/10$  alkali = 0.0247 grs. S.

In Germany the method due to Drehschmidt is usually employed.

The estimation is carried out by means of the apparatus shown in Fig. 103. The gas burner is encased in the manner shown in the figure, separate pipes, *a* and *b*, projecting from the casing for the supply of gas and air respectively to the burner. The air supply is purified

<sup>1</sup> *J. Soc. Chem. Ind.*, 1887, 5, 283.

<sup>2</sup> *Ibid.*, 1911, 30, 397.

from any sulphur dioxide present by passing up the tower B, containing pumice moistened with aqueous potassium hydroxide. The glass cylinder C is placed over the burner and fits a circular channel in the burner case, filled with mercury, thus preventing the admission of air at this point. The glass tube fused on to the cylinder C conveys the products of combustion to the train of wash-bottles D, each containing 20 c.c. of aqueous potassium hydroxide (5 per cent.), a little bromine

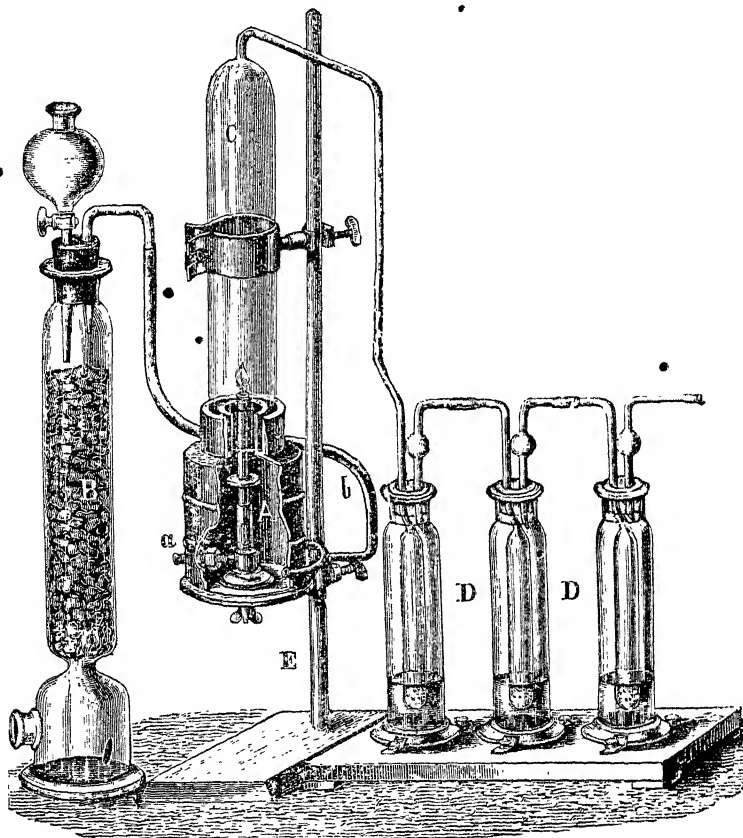


FIG. 108.

being added in the first two bottles, to ensure the complete oxidation of the sulphur dioxide.

In making a test, the burner is lighted and regulated to a consumption of  $\frac{2}{3}$  to 1 cb. ft. per hour; the outlet of the last wash-bottle is connected to a powerful water-pump so that a rapid current of air is drawn through the apparatus. The cylinder C is placed over the burner as the hand of the meter passes a suitable point, when the flame continues to burn quietly if the current of air is sufficiently rapid. At

the conclusion of the test the contents of the bottles D are washed out and the sulphur estimated as barium sulphate in the usual manner.

In place of the sodium hypobromite solution, hydrogen peroxide may be used in the wash-bottles, and the amount of sulphuric acid produced determined by titration with decinormal acid, as described in connection with the Referees' test. Pfeiffer employs a modified method in which the products of combustion are drawn through a known volume of decinormal sodium hydroxide solution to which neutral hydrogen peroxide solution (Merck's perhydrol) is added. The amount of alkali remaining at the end of the test is determined by titration with *N*/10 sulphuric acid, using dimethylaminoazobenzene as indicator.

Each c.c. of *N*/10 alkali neutralised is equivalent to 0.001603 g. or 0.02478 grain of sulphur, and the number of grains of sulphur per 100 cb. ft. is obtained by the equation:—

$$\text{grs. per 100 cb. ft.} = \frac{\text{Number of c.c. } N/10 \text{ NaOH} \times 0.02478 \times 100}{\text{Gas consumed corrected to N.T.P.}}$$

A quick method for the estimation of total sulphur, especially suitable for works' purposes, has recently been published by C. W. Somerville;<sup>1</sup> it depends on the estimation of the sulphur dioxide in the products of combustion of the gas by means of iodine and starch. The apparatus<sup>2</sup> in general construction resembles that of Drehschmidt (Fig. 103, p. 672), the gas being burned at the rate of about 0.5 cb. ft. per hour from a small burner, and the products of combustion aspirated by means of a water-pump through a wash-bottle of about 500 c.c. capacity containing 100 c.c. of *N*/1000 iodine solution diluted to 450 c.c., and a few cubic centimetres of starch solution. The wash-bottle is connected to the cylinder covering the flame as the meter hand passes a noted point, and the combustion products are allowed to pass through the solution until it is just decolorised, when the gas meter is at once by-passed. One hundred c.c. of *N*/1000 iodine solution contain 0.1268 g. of iodine, equivalent to 0.0016 g. or 0.024688 grain of sulphur, which is, therefore, the amount present in the volume of gas burned; from this the quantity of sulphur in 100 cb. ft. is readily calculated. The results obtained agree closely with those found simultaneously by gravimetric methods.

#### 10. Ammonia.

Of the total nitrogen present in the coal, only some 10 to 14 per cent. is obtained in the crude coal gas in the form of ammonia; the bulk of the remainder remains in the coke, and smaller quantities are obtained as gaseous hydrocyanic acid, free nitrogen, and as compounds

<sup>1</sup> *J. Gas Lighting*, 1910, 112, 29.

<sup>2</sup> Supplied by Messrs Townson & Mercer, Camomile St., London, E.C.

of nitrogen with carbon and hydrogen, such as pyridine and quinoline, which are found in the tar.

The removal of the ammonia from the crude gas commences as soon as the temperature has been sufficiently lowered to permit of the condensation of steam to water, and about one-half of the amount present is usually removed in the hydraulic main and condensers, the remainder being recovered by washing with weak liquor or fresh water in the washers or scrubbers. Where the latter part of the process is efficiently worked, the ammonia is reduced at the outlet of the apparatus to from 0.5 to 2.0 grains per 100 cb. ft.

The determination of the amount of ammonia present is readily carried out by passing a measured quantity of gas through two absorption bottles in series, each charged with a known volume of normal or decinormal sulphuric acid, and estimating the excess of acid at the end of the test by titration with standard alkali, using methyl orange as indicator. Unless the acid in the first absorption bottle is completely neutralised, practically the whole of the ammonia is retained in the first absorption bottle. In some cases a tube filled with broken glass, and moistened with a known volume of standard acid, is employed in place of the absorption bottles; where this is used, care must be taken to make sure that the glass has not an alkaline reaction by making a blank test; the glass beads supplied with such apparatus are often strongly alkaline, and neutralise appreciable quantities of acid, rendering the results obtained much too high.

With purified gas containing only a few grains of ammonia per 100 cb. ft., decinormal acid is used, and very accurate results are readily obtained, if care be taken that the tubes leading to the absorption bottles are of glass, with only a minimum of rubber connecting tubing.

For crude, unscrubbed gas normal acid must be employed, and in this case the above-named precautions are especially necessary, and the sample should always be taken by means of a tube projecting into the main, as described on p. 659; neglect of these precautions often leads to very incorrect figures. Even with these precautions, exact results are somewhat difficult to obtain on account of the tar-fog present in the gas, which also carries some condensed ammoniacal liquor with it. The solution in the bottles becomes contaminated with the tar, which makes the end-point of the titration more difficult to observe, and the ammoniacal liquor particles carried mechanically with the gas also neutralise some of the acid, thus making the results too high. If, on the other hand, an attempt be made to remove the tar-fog by a cotton-wool filter, the results are too low, as the filter also effects the removal of some of the ammonia from the gas stream. On the whole, it is best not to attempt to remove the tar-fog, and to allow for the fact that the tendency is then for the results to be rather too high.

When tar is present, it is sometimes found that the use of fluorescein as indicator, in place of methyl orange, is advantageous; the point of neutralisation is recognised by the disappearance of fluorescence, which is most readily observed if the glass vessel containing the liquid be placed on a sheet of glazed black paper.

With crude gas containing large quantities of ammonia, the quantity of gas required for a test is correspondingly small, and this is often conveniently measured by a graduated aspirator instead of by a meter; this procedure is generally necessary where the gas to be tested is under a pressure less than that of the atmosphere, the suction of the aspirator being utilised to draw the gas from the main through the absorption bottles. Where a meter is used, and the gas contains sulphuretted hydrogen, a small oxide purifier should be placed between the absorption bottles and the meter, as otherwise the metal work of the latter is rapidly corroded.

## II. Hydrocyanic Acid.

As mentioned under the estimation of ammonia, a small proportion of the nitrogen of the coal is converted into cyanogen derivatives, the amount formed varying to some extent with the nature of the coal, but more especially with the temperature to which the volatile products from the coal are heated during the distillation. The only cyanogen compound which has been detected with certainty in the gas is hydrocyanic acid, but it is possible that others, such as cyanogen itself, may be present in small quantity. Ammonium cyanide is not present as such in the gas, as it is completely dissociated into ammonia and hydrocyanic acid.

A part of the hydrocyanic acid is always removed in the hydraulic main and condensers as ammonium cyanide, and especially as thiocyanate, and no commercially practicable process for the recovery of this portion of the gas has yet been devised. Several different processes have, however, been adopted in certain works for the commercial recovery of the remainder, either in the form of ferrocyanides or thiocyanates (sulphocyanides). To obtain ferrocyanides the gas is washed with a mixture of ferrous hydroxide or carbonate and alkali; to obtain thiocyanates, with a solution of ammonium polysulphide which yields a concentrated solution of ammonium thiocyanate (British Cyanide Co.'s process).

Two types of ferrocyanide process are used. In the Rowland and Bueb processes the ammonia in the gas is used as the necessary alkali, which, with the ferrous hydroxide, yields a solution of ammonium ferrocyanide; this, however, is very unstable, and in presence of excess of iron salt is converted into insoluble double ferrocyanides of iron and ammonium. These, together with excess of iron sulphide formed from



the hydroxide, are filtered off, and the sludge sold for the manufacture of pure ferrocyanides and the recovery of the ammonia. In the second type of processes fixed alkalis are employed with the ferrous hydroxide (Knublauch and Foulis processes), which result in the recovery of the hydrocyanic acid chiefly as a solution of the ferrocyanide of the alkali used, from which the salts are obtained by evaporation and crystallisation.

If no special process is employed for the recovery of the cyanides the hydrocyanic acid is to a large extent removed from the gas in the ordinary processes of scrubbing and dry purification. A portion is absorbed in the scrubbers and converted into ammonium thiocyanate, which is absorbed in the ammoniacal liquor, where it has no commercial value. The remainder is largely taken up in the oxide of iron purifiers, partly as ammonium thiocyanate and partly as a mixture of iron ferrocyanides and double iron ammonium ferrocyanides, usually spoken of as "Prussian blue." When the quantity of ammonia passing into the purifiers is kept low, ferrocyanides are chiefly formed, and the spent oxide obtained frequently contains sufficient "blue" to make its recovery practicable, and it may be then sold on the value of its ferrocyanide content as well as for the sulphur present (*cf.* under Spent Oxide, p. 723).

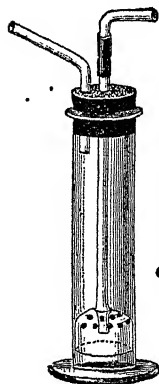


FIG. 104.

The amount of hydrocyanic acid in the gas, after condensation, varies generally from 75 to 125 grs. of HCN per 100 cb. ft., equivalent to 3 to 5 lbs. of crystallised sodium ferrocyanide,  $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ , per 10,000 cb. ft.

For the estimation of the amount of hydrocyanic acid in the gas, two methods are employed:—

- (i.) The gas is passed through a series of two or more absorption bottles, such as the one shown in Fig. 104, charged with a mixture of ferrous hydroxide and potassium hydroxide, prepared by mixing equal volumes of ferrous sulphate solution (1 : 10) and potassium hydroxide solution (1 : 3), the gas being passed at a rate of about 1 cb. ft. per hour, and measured in a meter in the usual manner. The contents of the absorption bottles are washed out at the end of the test, made up to a known volume, and an aliquot portion of the shaken mixture filtered from the insoluble black residue, which is washed free from ferrocyanide. The filtrate is treated with lead carbonate to remove sulphides, the filtered solution heated to  $60^\circ$ , and precipitated with hydrochloric acid and excess of ferric chloride; the precipitated Prussian blue is filtered off, preferably through a folded filter, the filtrate being returned to the filter until the precipitate no longer runs through. After washing once or twice with water, the filter paper and precipitate are placed in a beaker and decomposed by adding a slight excess of

potassium hydroxide, which converts it into potassium ferrocyanide, the ferric hydroxide also formed being filtered off and washed. For the determination of the amount of ferrocyanide in the filtrate this may be titrated with standard zinc or copper solutions, or the hydrocyanic acid contained may be determined by boiling with magnesium and mercuric chlorides, and subsequent acidification and distillation according to Feld's method. These methods are fully discussed in connection with the analysis of spent oxide (p. 726).

(ii.) In the second method, the hydrocyanic acid is absorbed by passing the gas through a series of three absorption bottles charged with a solution of ammonium sulphide and free sulphur; the ammonium polysulphide formed combines with the hydrocyanic acid, with the formation of ammonium thiocyanate. The gas is passed at the rate of about 1 cb. ft. per hour, and is measured as usual. At the end of the test the contents of the bottles are washed out, made up to a known volume, an aliquot portion of the solution treated with lead carbonate to remove sulphides, and, after filtering, a few crystals of sodium sulphite added, and the whole heated to  $80^{\circ}$ ; the liquid is then made faintly acid with sulphuric acid, and precipitated with an excess of copper sulphate solution, which throws down cuprous thiocyanate as a white precipitate, accompanied, however, by sulphides of copper, formed by the decomposition of the thiosulphate also present. The precipitate is filtered immediately, washed once or twice with water, and decomposed by the addition of 10 c.c. of a 10 per cent. solution of sodium hydroxide, free from chlorides. The sodium thiocyanate solution produced is filtered from the cuprous hydroxide and sulphide, the latter washed, the cold filtrate acidified with dilute nitric acid, and titrated with  $N/10$  silver nitrate solution using ferric alum solution as indicator, the complete precipitation of the thiocyanate being shown by the disappearance of the red colour of the ferric salt. Each c.c. of  $N/10$   $\text{AgNO}_3 = 0.007612$  g. of  $\text{NH}_4\text{CNS}$ , or  $0.002703$  g. of  $\text{HCN}$ .

The precipitation of the cuprous thiocyanate is necessary to remove the thiosulphates always present in the solution, and which if not eliminated, would also be precipitated by the silver nitrate. For most purposes this may be done more quickly and with sufficient accuracy, by the method proposed by Linder.<sup>1</sup> In this procedure the solution, after removal of sulphides by lead carbonate, is slightly acidified with sulphuric acid, heated to boiling, and 10 c.c. of a saturated solution of ferric alum added; after standing for five minutes, the liquid is cooled, acidified with nitric acid, and titrated with decinormal silver nitrate. The ferric alum converts the thiosulphate into tetrathionate, which does not affect the silver nitrate if the titration is carried out quickly.

The ferrocyanide method tends to give results which are slightly

<sup>1</sup> *Annual Report on Alkali, etc., Works*, 1906, p. 461.

low, as small quantities of the hydrocyanic acid are always converted into thiocyanate instead of into ferrocyanide, the amount of thiocyanate formed being greater when ammonia is present in the gas. On the other hand, the thiocyanate method tends to give results rather above the truth, as the carbon bisulphide also present in the gas is partially absorbed by the ammonium polysulphide with formation of ammonium thiocarbonates, which under certain conditions undergo decomposition into ammonium thiocyanate.

## 12. Naphthalene.

Naphthalene occurs in large quantity in the volatile products given off from the coal during distillation, but is almost completely removed during condensation, passing away with the tar, in which it is usually present in larger amount than any other single constituent. As, however, naphthalene has an appreciable vapour pressure at the ordinary temperature, the purified gas frequently contains small quantities, although the amount rarely exceeds from 15 grs. to 20 grs. per 100 cb. ft. Small though this quantity appears, it is frequently sufficient to cause serious trouble by its subsequent deposition in the solid state in the mains and services, both on the works and in the district of supply, and its estimation is, therefore, often a matter of importance.

No satisfactory, simple method of estimating the amount present in the hot gas has been devised, owing to the difficulty of separating the tar-fog without simultaneously effecting a partial removal of the naphthalene still present as vapour in the gas, but for the cooled gas free from tar-fog, several methods are used, all of which depend on the fact that naphthalene combines with picric acid to form the crystalline picrate,  $C_{10}H_8 \cdot C_6H_3N_3O_7$ , which is practically insoluble in saturated picric acid solution, although it is partly dissociated into its constituents by water.

Colman and Smith<sup>1</sup> pass the gas through a series of three absorption bottles, charged with a nearly saturated solution of picric acid of known strength (about  $\frac{1}{20}$ th normal), 100 c.c. being used altogether. The gas, previously passed through an absorption bottle charged with citric acid solution to remove ammonia, which would otherwise neutralise some of the picric acid, is bubbled through the latter at the rate of 0.5 to 1.0 cb. ft. per hour. The whole of the naphthalene is thereby removed from the gas (the first absorption bottle removing all but traces), and separates as naphthalene picrate, which, however, undergoes a partial dissociation into free naphthalene and picric acid. To effect the complete conversion of the naphthalene into the picrate, Küster's method<sup>2</sup> is adopted. The contents of the absorption bottles are washed with as small a quantity of water as possible into a narrow-mouthed bottle of

<sup>1</sup> *J. Soc. Chem. Ind.*, 1900, 19, 128.

<sup>2</sup> *Ber.*, 1894, 24, 1101.

such size that it is nearly filled with the liquid; this is then closed by a rubber cork, fitted with a glass stopcock or similar device, the bottle evacuated, and placed in a bath of cold water and heated, with occasional shaking, until the whole of the picrate has dissolved. On cooling, the whole of the naphthalene then separates as the picrate; occasional shaking during cooling is necessary to prevent the sublimation of naphthalene on to the upper surface of the bottle.

As naphthalene picrate is partly dissociated by water, the precipitate should be washed as little as possible with water, otherwise too low results are obtained. To avoid washing entirely, the contents of the bottle are poured into a measuring cylinder, and the volume noted; it is then filtered through a dry filter paper, the first few cubic centimetres of filtrate rejected, and 100 c.c. of the filtrate titrated with  $N/10$  sodium hydroxide, using phenolphthalein or lacmoid as indicator. The former shows only the yellow colour of picric acid when acid, changing to a reddish yellow when alkaline; with lacmoid the colour is reddish brown when acid, changing to green when alkaline.<sup>1</sup>

If  $n$  = volume in cubic centimetres of the liquid after heating, and  $v$  the number of c.c. of  $N/10$  NaOH required for 100 c.c. of the filtrate, the volume of  $N/10$  alkali required for the whole solution is  $\frac{n \times v}{100} = V$ .

The alkali-equivalent of the 100 c.c. of picric acid originally taken, termed  $V^1$ , is ascertained by titration with  $N/10$  NaOH in a similar manner, and the difference between the two figures,  $V^1 - V$ , shows the quantity of  $N/10$  alkali corresponding to the amount of picric acid which has been removed by combination with the naphthalene. One c.c. of decinormal solution corresponds to 0.0229 g. of picric acid, and therefore to 0.0128 g. or 0.1975 grain of naphthalene, as 229 parts of picric acid combine with 128 parts of naphthalene. The number of grains of naphthalene per 100 cb. ft. is:—

$$\frac{(V^1 - V) \times 100 \times 0.1975}{\text{Vol. of gas passed}} = \text{grains } C_{10}H_8 \text{ per 100 cb. ft.}$$

A modified method, which is sometimes convenient, though rather less accurate, is to filter off the naphthalene picrate which separates after the heating process, with the aid of a pump, wash once with a small quantity of water, then wash the precipitate from the filter paper into a flask, heat till all is dissolved, and titrate the hot solution with  $N/10$  alkali. The alkali used should be identical with the figure  $V^1 - V$  above, and the quantity of naphthalene is calculated by the same equation. Slightly lower results are usually obtained in this manner.

Jorissen and Rutten<sup>2</sup> emphasise the fact that low results are

<sup>1</sup> Observers having a tendency to colour blindness often cannot employ lacmoid, as they are unable to observe the change to green at all, or only very indefinitely.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1909, 28, 1179.

obtained by the foregoing method if the naphthalene picrate is washed with much water. They find further that when a saturated solution of picric acid containing also solid picric acid is employed, the naphthalene picrate is directly precipitated from the gas as undissociated picrate. They, therefore, recommend the following procedure:—

Two hundred and fifty c.c. of a saturated solution of picric acid are evaporated to about 150 c.c. and transferred, while hot, to two absorption bottles. The gas, previously freed from tar-fog, cyanogen, sulphuretted hydrogen, and ammonia, is passed through the bottles at the rate of about 1.5 cb. ft. per hour, until a fair quantity of picrate has been formed in the first bottle. The solution and precipitate are then washed into a flask, made up to 250 c.c., the closed flask heated to 40° for about half an hour, and shaken from time to time till all the picrate has dissolved. After cooling, the solution is filtered from the separated naphthalene picrate, and an aliquot portion of the filtrate titrated with *N*/10 alkali, the same volume of the original solution being also titrated. From the difference between the two titrations the amount of naphthalene is readily calculated in a similar manner to that given in the previous method.

C. J. Dickenson Gair<sup>1</sup> passes the gas through two absorption bottles containing 350 c.c. of diluted acetic acid of sp. gr. 1.044, at the rate of 1 cb. ft. per hour. At the conclusion of the test, 500 c.c. of saturated picric acid solution are added, the dissolved naphthalene being precipitated as picrate, which is filtered off on the pump, using a dry, weighed filter, washed with saturated picric acid solution, and finally once with water. The filter paper and precipitate are dried quickly in vacuo over sulphuric acid, and weighed. The weight of naphthalene picrate found, multiplied by  $\frac{128}{128+229} = 0.3585$ , gives the weight of naphthalene in the volume of gas passed. Or, the precipitate may be washed into a flask, and titrated in hot solution with *N*/10 alkali, as previously described.

With cooled but unpurified gas containing hydrocyanic acid and sulphuretted hydrogen, these impurities are apt to affect the picric acid to some extent; where the estimation of naphthalene in such gas is required, the absorption by acetic acid is preferable.

The employment of alcohol to wash the naphthalene from the gas and subsequent precipitation of the solution with aqueous picric acid, has not proved successful, as under these conditions some of the other vapours present in the gas, such as the xylenes, also form crystalline picrates, and too high results are, therefore, obtained.

<sup>1</sup> *J. Soc. Chem. Ind.*, 1905, 24, 1279; 1907, 26, 1263.

### 13. Tar-fog.

The tarry constituents of the hot gas issuing from the retort separate on cooling, for the most part, as a dense fog of finely divided tar particles, which gradually coalesce and are removed by subsidence and by friction with the surfaces of the apparatus through which the gas passes. But even when the gas is completely cooled, a certain proportion of the fog is still left in the gas, and if allowed to go forward with the gas, is deposited in the washing plant and in the purifiers. In the former, and especially in coke scrubbers, the deposited tar interferes considerably with the proper removal of the ammonia, and when filtered out by the oxide of iron in the purifiers, it impairs the power of the latter to remove sulphuretted hydrogen, increases the back pressure exerted by the mass, and also diminishes the value of the resulting spent oxide, and renders it more difficult to work this up to a high percentage of sulphur. A suitable form of tar separator is, therefore, usually placed after the condensers. Two types of apparatus are in common use; the first, represented by the Pelouze-Audouin condenser, effects the removal of the fog by dividing up the gas into very fine streams, each of which impinges at a high velocity against an iron plate, whilst in the second, represented by the Livesey washer, the gas is made to bubble in fine streams through weak ammoniacal liquor, whereby the tar-fog is largely removed, and the weak liquor simultaneously concentrated.

The estimation of the quantity of tar-fog present at different points of the system is, therefore, frequently of importance, and is conveniently made by the method proposed by Clayton and Skirrow.<sup>1</sup> For this purpose a long glass tube  $\frac{3}{4}$  inch in external diameter is taken, a small hole  $\frac{1}{4}$  inch in diameter blown near one end, and about 12 inches of the tube above this hole filled with loosely packed cotton wool, which has been previously extracted with carbon bisulphide to remove fatty matter. The end of the tube near the small side hole is closed by a cork, and the tube inserted through a cork placed in a  $1\frac{1}{2}$ -inch cock on the main conveying the gas, and so fixed that the small side hole faces the gas stream as nearly as possible two-thirds across the main, or one-third of the diameter from the side opposite to the cock through which it is inserted, this being the point of mean velocity of gas in the main. The whole of the filtering material should be within the main, so that it is kept at the same temperature as the gas to avoid condensation, and the gas is allowed to pass through the filter at such a rate that the gas velocity through the  $\frac{1}{4}$ -inch hole is greater than that of the gas in the main. It is only by observing these precautions that it is possible to obtain uniform results.

<sup>1</sup> *J. Gas Lighting*, 1907, 98, 660.

The gas, after passing through the filter, is purified by oxide of iron, from sulphuretted hydrogen, and measured in a meter, from 20 to 30 cb. ft. being passed. The tube is then removed from the main, the external surface wiped clean from tar, and the cotton wool containing the tar placed in a Soxhlet tube and extracted with carbon bisulphide, in a tared flask. The carbon bisulphide extract is evaporated off on the water-bath, dry air finally drawn through the flask for half a minute, and the flask again weighed. From the weight of tar and the volume of gas passed, the amount of tar-fog in 1 or 100 cb. ft. is readily calculated.

The free carbon in the tar remains undissolved in the cotton wool and some of the low-boiling constituents of the tar are evaporated with the carbon bisulphide, so that the results are below the exact figure, but the figures obtained are fairly comparative and sufficiently exact for most practical purposes.

According to Feld's method,<sup>1</sup> the gas drawn from the main, as already described, is passed through a weighed U-tube containing cotton wool. Before weighing, the latter is placed in a water-bath warmed to the temperature of the gas in the main, and the gas passed through it, after traversing two additional U-tubes placed in the same bath and filled with cotton wool (unweighed) and calcium chloride respectively, until its weight is constant. The weighed tube is then connected directly with the tar-laden gas stream and a measured volume of gas passed. The tube is then reconnected to the outlet of the two U-tubes previously employed, and the gas again passed until the weight of the tar-absorption U-tube is constant; the increase of weight gives the amount of tar-fog in the volume of gas passed. Working in this manner, the moisture in the filtered tar is removed without simultaneous loss of tar vapours, as the gas employed is always saturated with tar vapours at the temperature of the water in the bath, and in the gas main.

#### IV.—THE SPECIFIC GRAVITY OF GAS

A knowledge of the specific gravity of gas mixtures affords valuable information, and its determination is accordingly of importance, provided it can be effected by simple methods. A continuous record of the specific gravity of the gas made is not only of statistical value, but also gives some information concerning changes in composition, but it is to be borne in mind that the origin of a change in specific gravity may be uncertain; the specific gravities of ethylene and of nitrogen, for instance, are almost identical. As affecting gas supply, a knowledge of the specific gravity of illuminating gas is of value because the quantity of

<sup>1</sup> *J. Gasbeleucht.*, 1911, 54, 33.

gas issuing from an orifice at constant pressure varies indirectly with the square root of the specific gravity, and the same holds with regard to the capacity of the mains for the delivery of gas under constant pressure. Further, in the distribution system, the relative pressure of the gas to the atmosphere increases with increasing altitude, the increase being greater the lower the specific gravity of the gas. Where districts of very different levels have to be supplied, this has to be taken into account. In the use of gas for the filling of balloons, the specific gravity is, of course, of primary importance.

### 1. Calculation of the Specific Gravity from the Analysis.

The specific gravity of a gas, the composition of which is known, may be calculated by multiplying the percentage of each constituent by its known specific gravity and dividing the sum of the products by 100, as shown in the following example:—

	Per cent. by vol.		Sp. gr. at 0° C. and 760 mm.		Multi- plier.
CO <sub>2</sub>	= 1.2	×	1.5290	=	1.8348
C <sub>n</sub> H <sub>m</sub>	= 3.4	×	1.4595	=	4.9623
O <sub>2</sub>	= 0.3	×	1.1049	=	0.3315
CO	= 6.8	×	0.9671	=	6.5763
CH <sub>4</sub>	= 32.9	×	0.5590	=	18.3911
H <sub>2</sub>	= 49.2	×	0.0695	=	3.4194
N <sub>2</sub>	= 6.2	×	0.9721	=	5.9970
					<hr/> 41.5124 ÷ 100 = 0.4151

The specific gravity of a dry gas of this composition at 0° and 760 mm. would, therefore, be 0.415, and the specific gravity at any other temperature of the dry or moist gas can be calculated therefrom in the usual manner. In making this calculation, the usual approximate assumption is made that the unsaturated hydrocarbons present are equivalent to an equal volume of propylene, the sp. gr. of which is 1.4595. Where the amounts of ethylene and benzene have been separately determined, the percentages of these and their specific gravities may be employed in the calculation.

### 2. Experimental Determination of the Specific Gravity.

For accurate determinations, Dumas' method of directly weighing the gas in glass vessels of known capacity is to be recommended.<sup>1</sup> In technical work, however, simpler methods are made use of.

Of such methods, that devised by Bunsen<sup>2</sup> depends on the different rates of effusion of equal gas volumes through a fine opening, in which

<sup>1</sup> Cf. F. Kohlrausch, *Introduction to Physical Measurements*, trans. by H. R. Procter and T. Waller, 3rd edition, 1894; also Slaby, *J. Gasbeleucht.*, 1890, 33, 157.

<sup>2</sup> *Gasometrische Methoden*, 2nd edition, 1877, p. 184.



case the specific gravities of any two gases are related to each other as the squares of their rates of effusion. When compared with air, as is always done in practical work, the specific gravity of the latter is denoted by 1 and is thus eliminated from the calculation. Thus, if the time of effusion is found to be  $g$  seconds and that of an equal volume of air 1 second, then the

$$\text{Specific gravity of the gas} = \frac{g^2}{1^2}$$

(i.) *Schilling's Apparatus*<sup>1</sup> for determining the specific gravity

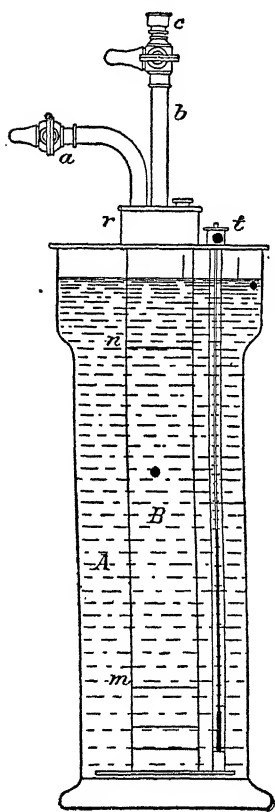


FIG. 105.

(Fig. 105) has been evolved from Bunsen's apparatus, which it has completely displaced. It consists of a large glass cylinder, A, about 40 cm. high, in which a smaller cylinder, B, is suspended and kept in position at the top by the metal frame  $r$ , which rests with three arms on the rim of the cylinder and also carries the thermometer  $t$ ; B is open at the bottom and is fixed just free from the base of A, where it is again centred by a metal frame with three arms. The tubes  $a$  and  $b$  fixed on the metal frame are provided with stopcocks and serve for the admission and expulsion of the gas;  $b$  has a three-way stopcock which can be turned so as to communicate either with  $b$  or  $c$ . The headpiece  $c$  is fitted with a small thin platinum disc placed horizontally, with an extremely fine opening in the middle, which is made by piercing the foil with a needle and then hammering it out; to protect it from dust, etc., a cap is screwed on the head  $c$  when the apparatus is not in use.

For the determination, the vessel A is filled with so much water that there is just sufficient room for the introduction of the cylinder B when filled with air and suspended therein. As soon as the water has come to rest the time of effusion of the volume of air between the marks  $m$  and  $n$  is determined; these marks go right round the cylinder; according to Pannertz, bands of fine cord round the marks permit of greater accuracy of observation. The stopcock on  $b$  is first turned so as to communicate with the head  $c$ ; the level of the water in the lower part of the cylinder B then begins to rise as it displaces the air, and the time is taken with a stop-watch as soon as the meniscus passes the mark  $m$ ;

<sup>1</sup> *Handbuch für Gasbeleucht.*, 3rd edition, p. 301.

a similar reading is taken when the meniscus of the water passes  $n$  and the total time noted. The residual air in the cylinder is then displaced by the gas to be examined by connecting the stopcock  $a$  with the supply, and opening  $b$ ; the gas is allowed to pass through for about two minutes. The displacement of the air is accelerated by slowly raising the cylinder almost completely out of the water and lowering it again. The outlet of  $b$  is then closed, the cylinder again raised in order to fill it completely with gas, the inlet of  $a$  closed, and the cylinder again placed in position. After the water has come to rest, the time of effusion of the gas is measured under exactly the same conditions as with the air, so that the time of effusion of equal volumes of gas and air, measured between  $m$  and  $n$ , is ascertained. The calculation of the specific gravity is then made according to the formula given above.

As the air and gas are both measured saturated with moisture and at the temperature of the water by which they are confined, all corrections with respect to vapour tension and temperature are obviated. It is well, however, to read the temperature by the thermometer  $t$  before and after the experiment, as a check. In exact work the test should be repeated; the times observed in the duplicate tests should not differ from each other by more than 0.2 second. The following is an example of the determination of the specific gravity of coal gas:—

$$\begin{aligned} \text{Time of effusion observed for gas} &= 2' 25.1'' = 145.1'' \\ \text{'' air} &= 3' 40.8'' = 220.8'' \\ \text{Specific gravity} &= \frac{145.1^2}{220.8^2} = 0.4321 \end{aligned}$$

A table of co-ordinates for coal gas have been drawn up by P. Krug, on the suggestion of Pfeiffer,<sup>1</sup> which permits of a direct reading of the specific gravity from the times of effusion.

The results obtained with Schilling's apparatus are reliable to the third decimal place.<sup>2</sup> This method for ascertaining the specific gravity is always to be preferred when accuracy is important, as, for example, in the calculation of the calorific value from the analysis.

(ii.) *The Lux Gas Balance.*<sup>3</sup> This apparatus is especially useful for gasworks practice, as it indicates the specific gravity of the gas directly. It depends on the simple principle of directly weighing equal volumes of air and gas, the difference of which in weight is shown as specific gravity (air = 1) by the displacement on a scale. The globe-shaped receiver (Fig. 107), which may be made of glass, balances with the beam on two steel points  $s, s$ , (Fig. 106), which move in a hollow, conical steel groove. The fork-shaped end of the pillar carries the gas inlet and outlet  $r$ , and  $o$ , which communicate with the small cups  $p$  and  $p_1$ , which are filled with mercury. Two small tubes are attached to the

<sup>1</sup> *J. Gasbeleucht.*, 1887, 30, 251; 1903, 46, 481.

<sup>2</sup> A "Specific Gravity Bell," depending on the same principles as the above apparatus, is made by Messrs A. Wright & Co., Westminster.

<sup>3</sup> *J. Gasbeleucht.*, 1887, 30, 251.

beam of the balance at right angles to the plane of swing, the ends of which are bent at right angles and are connected with the inlet and outlet of the pillar by the mercury seal of the cups  $p$  and  $p_1$  without interfering with the movement of the beam. One of the small tubes

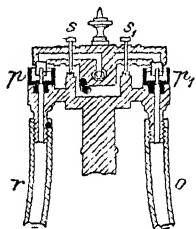


FIG. 106.

conducts the gas into the globe through a central tube, whilst the other serves as the exit tube.

The balance is mounted in a glass case provided with a door. The gas inlet and outlet to  $r$  and  $o$  are connected by two small tubes, each fitted with a stop-cock and rubber connection, on one of the ends of the balance case. The beam of the balance is divided into 100 divisions, and from each 10 to the next, reckoned from the pivot, there are graduations, 0.0, 0.1, 0.2...1.0; the beam carries a nickel rider. The graduated arc is divided into fifty parts, the middle of which is the zero; the graduations, 0.1, 0.2, etc., are placed above and below from each 10 to the next; the marks below zero are negative values.

The balance must be fixed in a position that is not subject to

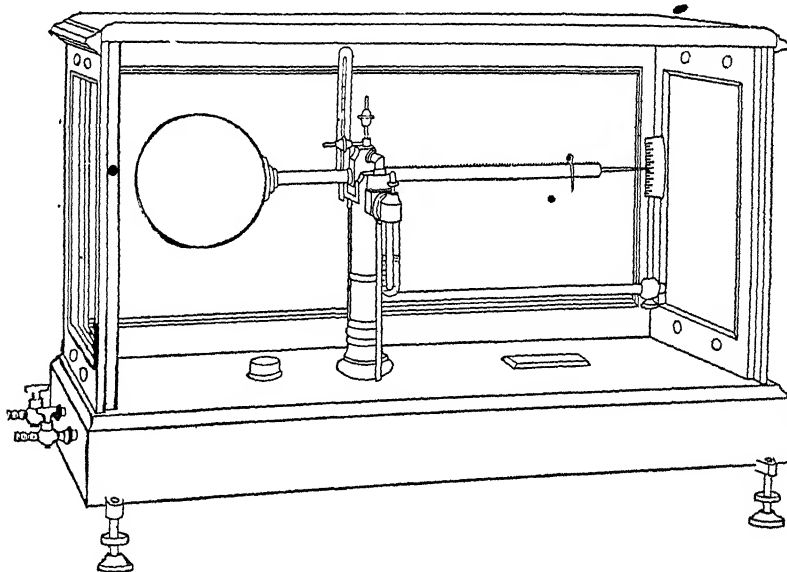


FIG. 107.

vibration, nor exposed to direct sunlight or other sudden changes of temperature. When at rest, the beam of the balance rests firmly on the pillar; it is released by means of a screw at the right-hand end of the case. When the globe is filled with air and the rider is on the outermost mark 1, the pointer should come to rest exactly on the zero mark.

The adjustment of the balance beam is effected by means of a small

screw above the middle of the beam, which can be moved horizontally; for further adjustment, the rider is placed on the division 0.8. If the balance has the right sensitiveness, each degree on the graduated arc should correspond to each degree on the beam; the pointer ought then to come to rest at +0.2 on the arc. This adjustment is made by means of the small screw, which can be moved vertically over the middle of the beam.

To ascertain the specific gravity of the gas to be tested, the air is first displaced from the balance by passing the gas through for five minutes. The rider is then placed on the graduation regarded as likely to be nearest to the specific gravity of the gas, for example, 0.4; the beam is then released and the division on the graduated arc on which the pointer comes to rest after swinging up and down is read. This reading, added to or subtracted from that of the rider, gives the second decimal for the specific gravity; the reading -0.01, would, for instance, indicate a specific gravity of  $0.40 - 0.01 = 0.39$ . The third decimal place can be estimated; a greater degree of accuracy in the determination is not to be expected.

A table of corrections for barometric pressure and temperature is provided, however, for the apparatus, which influences the results to the fourth place of decimals. A correction of this kind is theoretically necessary on account of the nature of the balance. If, for example, the atmospheric pressure increases, the gas in the globe of the balance as well as the surrounding air is contracted, so that the weight of the contents of the globe, and that of the air displaced thereby, both increase; accordingly the globe of the balance tends to become heavier by the increasing weight of the gas, and lighter in proportion to the greater upward push of the air. Since the absolute increase in weight is greater with air than with gas, in proportion to the difference in their specific gravities, therefore the globe containing the gas becomes relatively lighter with an increase in pressure and heavier with a decrease in pressure. The necessary correction for the influence of changes of pressure is to add 0.0007 for every millimetre of pressure over 760 mm., and to subtract 0.002 for every degree above 15°, and *vice versa*.

For example, the specific gravity of a gas was found by the balance to be +0.41 at 28° and 775 mm. pressure:—

$$\begin{aligned} 775 - 760 &= 15; +0.0007 \times 15 = +0.0105 \\ 28 - 15 &= 13; -0.002 \times 13 = -0.0260 = -0.0155 \\ \text{Corrected sp. gr.} &= 0.3945. \end{aligned}$$

A table supplied with the apparatus gives the corrections from 0° to 30° C. and from 730 to 790 mm.; it is, however, applicable only for gases of specific gravity between 0.4 and 0.5.

For rapid tests following closely on each other, the apparatus gives

satisfactory results to the second decimal place; after any considerable interval, however, say, from one day to another, a new adjustment will be necessary, as a rule, on account of the unequal expansion of the dissimilar arms of the beam with changes of temperature, for which no compensation is provided.

Apparatus for the determination of the specific gravity of gases by measurement, with a delicate differential pressure gauge, of the difference between the statical pressure of a long vertical column of gas and a column of air of equal length have been devised by Krell<sup>1</sup> and by Threlfall.<sup>2</sup> These are capable of giving very accurate results, but are too large for general employment in an ordinary laboratory.

#### V.—THE CALORIFIC AND ILLUMINATING POWER OF GAS

The value of gas to a consumer depends chiefly upon its calorific and illuminating power. Up to about thirty years ago, only the latter quality was of material importance, as the great bulk of the gas then supplied was used for illumination purposes, with the employment of open flame burners. At the present time, however, a very large proportion of the gas supplied is used for gas fires, cookers, and gas engines; for such purposes the calorific power of the gas is the point of chief importance, the illuminating power not coming into consideration. Even for illumination, this is now also the case, as the great bulk of the gas employed for this purpose is burned in incandescent burners, so that the illumination is mainly dependent on the calorific power of the gas and on the flame temperature, and quite independent of the illuminating power as such. It is estimated that not more than 10 per cent. of the gas supplied in this country is now used in open flame burners, and on the Continent the proportion is still smaller.

At the present time, therefore, the calorific power is by far the most important factor in the valuation of coal gas, but owing to the fact that the various Gas Undertakings are still statutorily compelled to supply gas of the illuminating power specified in their respective Acts of Parliament, it is this latter value which is mostly determined. It is probable, however, that a calorific power standard will be substituted before very long for the illuminating power standard, as has already been done to a very large extent in Germany.

The illuminating power of a gas is in no way an absolute quality of the gas, such as its specific gravity, but varies greatly according to the construction of the burner employed, the rate at which it is burned, and to a smaller extent, with the atmospheric temperature and pressure;

<sup>1</sup> *J. Gasbeleucht.*, 1899, 42, 212.

<sup>2</sup> *Proc. Roy. Soc., A*, 1906, 77, 542; *J. Soc. Chem. Ind.*, 1907, 26, 359.

the actual luminosity depends mainly upon the extent to which solid carbon particles are deposited in the flame and the temperature to which these are raised. For the determination of illuminating power, therefore, it is necessary to carry out the test under certain specified conditions, which are usually laid down in the special Acts of the various Undertakings. Unfortunately, the conditions specified vary very greatly in the case of different works, so that the results obtained in such cases are frequently quite incomparable (p. 706).

The calorific power, on the other hand, is an absolute quality of the gas. It represents the total potential energy of the gas, expressed in heat units, and provided that combustion is complete, the calorific power remains the same whatever burner is employed, and whatever the rate of combustion.

Under these conditions, it is evident that there can be no exact relationship between the illuminating and calorific power of different samples of gas. In the case, however, of gases of the same general composition, such as unmixed coal gas, it is found that, generally speaking, the calorific power increases with the illuminating power, but at a much slower rate, and *vice versa* diminishes with decreasing illuminating power, but again at a much slower rate, so that gas which has been deprived of all illuminating power, when burned in a flat flame, has still a relatively high calorific power. The same is true of carburetted water gas by itself, but the calorific power of this gas is some 10 to 15 per cent. lower than that of coal gas having the same illuminating power, if the latter be determined in both cases by a method which enables true relative values to be obtained.

#### A. DETERMINATION OF THE CALORIFIC POWER

In this country the unit of heat employed is the British Thermal Unit (usually denoted B.Th.U. to distinguish it from the electrical Board of Trade Unit, for which the contraction B.T.U. is employed); it is the quantity of heat required to raise 1 lb. of water 1° F. The calorific power of a gas is usually given by stating the number of B.Th.U. evolved in the combustion of 1 cb. ft. of the gas. On the Continent, the heat unit employed is the larger calorie (Cal.), and the results are given as calories per cubic metre. The calorific power tests of London gas, carried out under the instruction of the Metropolitan Gas Referees, are recorded in calories per cubic foot.

For conversion of calories into B.Th.U., the factor is 3.968; that for converting calories per cubic meter into B.Th.U. per cubic foot is 0.1124.

In the experimental determination of the calorific power of any gas containing hydrogen, the water vapour produced by the combustion

Tabular Numbers, being a Table to facilitate the Correction  
peratures and under different Atmospheric Pressures

BAR.	THERMOMETER—			FAHRENHEIT.			50°	52°	54°	56°	58°	60°
	40°	42°	44°	46°	48°	50°						
28.0	.979	.974	.970	.965	.960	.956	.951	.946	.942	.937	.932	
28.1	.983	.978	.973	.969	.964	.959	.955	.951	.945	.941	.936	
28.2	.986	.981	.977	.972	.967	.963	.958	.953	.949	.944	.939	
28.3	.990	.985	.980	.976	.971	.966	.961	.957	.952	.947	.942	
28.4	.993	.988	.984	.979	.974	.970	.965	.960	.955	.951	.946	
28.5	.997	.992	.987	.983	.978	.973	.968	.964	.959	.954	.949	
28.6	1.001	.995	.991	.986	.981	.977	.972	.967	.962	.958	.953	
28.7	1.004	.999	.994	.990	.985	.980	.975	.970	.966	.961	.956	
28.8	1.007	1.003	.998	.993	.988	.984	.979	.974	.969	.964	.959	
28.9	1.011	1.006	1.001	.997	.992	.987	.982	.977	.973	.968	.963	
29.0	1.014	1.010	1.005	1.000	.995	.990	.986	.981	.976	.971	.966	
29.1	1.018	1.013	1.008	1.004	.999	.994	.989	.984	.979	.975	.969	
29.2	1.021	1.017	1.012	1.007	1.002	.997	.992	.988	.982	.978	.973	
29.3	1.025	1.020	1.015	1.011	1.006	1.001	.996	.991	.986	.981	.976	
29.4	1.028	1.024	1.019	1.014	1.009	1.004	.999	.995	.990	.985	.980	
29.5	1.032	1.027	1.022	1.018	1.013	1.008	1.003	.998	.993	.988	.983	
29.6	1.036	1.031	1.026	1.021	1.016	1.011	1.006	1.001	.996	.992	.986	
29.7	1.039	1.034	1.029	1.025	1.019	1.015	1.010	1.005	1.000	.995	.990	
29.8	1.043	1.038	1.033	1.028	1.023	1.018	1.013	1.008	1.003	.998	.993	
29.9	1.046	1.041	1.036	1.031	1.026	1.022	1.017	1.012	1.007	1.002	.997	
30.0	1.050	1.045	1.040	1.035	1.030	1.025	1.020	1.015	1.010	1.005	1.000	
30.1	1.053	1.048	1.043	1.038	1.033	1.029	1.024	1.019	1.014	1.009	1.003	
30.2	1.057	1.052	1.047	1.042	1.037	1.032	1.027	1.022	1.017	1.012	1.007	
30.3	1.060	1.055	1.050	1.045	1.040	1.036	1.030	1.025	1.020	1.015	1.010	
30.4	1.064	1.059	1.054	1.049	1.044	1.039	1.034	1.029	1.024	1.019	1.014	
30.5	1.067	1.062	1.057	1.052	1.047	1.042	1.037	1.032	1.027	1.022	1.017	
30.6	1.071	1.066	1.061	1.056	1.051	1.046	1.041	1.036	1.031	1.026	1.020	
30.7	1.074	1.069	1.064	1.059	1.054	1.049	1.044	1.039	1.034	1.029	1.024	
30.8	1.078	1.073	1.068	1.063	1.058	1.053	1.048	1.043	1.037	1.032	1.027	
30.9	1.081	1.076	1.071	1.066	1.061	1.056	1.051	1.046	1.041	1.036	1.031	
31.0	1.085	1.080	1.075	1.070	1.065	1.060	1.055	1.049	1.044	1.039	1.034	

\* \* The numbers in the above table have been calculated from the formula  $n = \frac{17.64(h-a)}{460+t}$   
scale, and  $a$  the tension of aqueous vapour at  $t^\circ$ . If  $v$  is any volume at  $t^\circ$ , and  $h$  inches

of the Volume of Gas measured over Water at different Tem-  
to the Volume at 60° F. and 30 in. pressure (moist).

62°	64°	66°	68°	70°	72°	74°	76°	78°	80°	82°	84°
.927	.922	.917	.912	.907	.902	.897	.892	.887	.881	.875	.870
.930	.926	.921	.916	.911	.905	.900	.895	.890	.884	.879	.873
.934	.929	.924	.919	.914	.909	.904	.898	.893	.887	.882	.876
.937	.932	.928	.922	.917	.912	.907	.902	.896	.891	.885	.880
.941	.936	.931	.926	.921	.915	.910	.905	.900	.894	.888	.883
.944	.939	.934	.929	.924	.919	.914	.908	.903	.897	.892	.886
.947	.943	.938	.932	.927	.922	.917	.912	.906	.901	.895	.889
.951	.946	.941	.936	.931	.925	.920	.915	.909	.904	.898	.893
.954	.949	.944	.939	.934	.929	.924	.918	.913	.907	.901	.896
.958	.953	.948	.942	.937	.932	.927	.921	.916	.910	.905	.899
.961	.956	.951	.946	.941	.935	.930	.925	.919	.914	.908	.903
.964	.959	.954	.949	.944	.939	.933	.928	.923	.917	.911	.906
.968	.963	.958	.952	.947	.942	.937	.931	.926	.920	.914	.909
.971	.966	.961	.956	.950	.945	.940	.935	.929	.923	.918	.912
.975	.969	.964	.959	.954	.949	.943	.938	.932	.927	.921	.915
.978	.973	.968	.962	.957	.952	.947	.941	.936	.930	.924	.919
.981	.976	.971	.966	.960	.955	.950	.944	.939	.933	.927	.922
.985	.980	.974	.969	.964	.959	.953	.948	.942	.937	.931	.925
.988	.983	.978	.972	.967	.962	.957	.951	.946	.940	.934	.928
.991	.986	.981	.976	.970	.965	.960	.954	.949	.943	.937	.932
.995	.990	.985	.979	.974	.968	.963	.958	.952	.946	.941	.935
.998	.993	.988	.983	.977	.972	.966	.961	.955	.950	.944	.938
1.002	.996	.991	.986	.980	.975	.970	.964	.959	.953	.947	.941
1.005	1.000	.995	.989	.984	.978	.973	.968	.962	.956	.950	.945
1.008	1.003	.998	.993	.987	.982	.976	.971	.965	.959	.954	.948
1.012	1.006	1.001	.996	.990	.985	.980	.974	.969	.963	.957	.951
1.015	1.010	1.005	.999	.994	.988	.983	.977	.972	.966	.960	.954
1.018	1.013	1.008	1.003	.997	.992	.986	.981	.975	.969	.963	.957
1.022	1.017	1.011	1.006	1.000	.995	.990	.984	.978	.972	.967	.961
1.025	1.020	1.015	1.009	1.004	.998	.993	.987	.982	.976	.970	.964
1.029	1.023	1.018	1.013	1.007	1.002	.996	.991	.985	.979	.973	.967

where  $h$  is the height of the barometer in inches,  $t$  the temperature on the Fahrenheit pressure, and  $V$  the corresponding volume at 60° and 30 inches pressure,  $V = v_m$ .



is condensed to liquid water in the calorimeter, and the latent heat of such steam is, therefore, always included in the observed calorific power, which is known as the *Gross Calorific Power*. This latent heat can, however, only be utilised in practice in the very exceptional cases where the products of combustion are completely cooled to atmospheric temperature. It is, of course, never evolved in the flame itself, and takes no part in the development of the flame temperature, nor is it evolved in the cylinder of a gas engine, and is, therefore, unavailable for the production of mechanical energy. From the point of view of thermodynamics, therefore, it is important to know the amount of such unavailable latent heat. As the latent heat of steam is known (viz., 0.537 Cal., or 2.13 B.Th.U. for each cubic centimetre or gram of water condensed), the total latent heat is readily ascertained by collecting and measuring the amount of condensed water obtained during the test, and multiplying the number of cubic centimetres found, per cubic foot, by one or other of these values, according as the results are being returned in Cal. or B.Th.U. The amount thus found, deducted from the gross value, gives the *Nett Calorific Power*.

It is to be borne in mind that the latent heat of the steam is not the only heat evolved by the combustion of the gas which is not utilised in practice, for, as the products of combustion, together with an excess of air, mostly pass away at a temperature much exceeding that of the atmosphere, the sensible heat of these products is also wasted, and this often amounts to more than that of the latent heat of the steam.

As the results are given for unit volume of the gas, it is also necessary to define the standard temperature and pressure at which the gas is measured. As already stated (p. 625), the standard conditions in this country are that the gas shall be measured moist at 60° F., and 30 in. pressure. A table<sup>1</sup> for obtaining the volume of a gas under these conditions from its volume at temperatures of from 40° to 80° F. and from 28.0 to 31 in. pressure, is given on pp. 690-91.

In Germany, the results are sometimes given for dry gas at 0° C., and sometimes for moist gas at 15° C. and 760 mm. (the latter conditions are practically identical with the British conditions of moist gas at 60° F. and 30 in.), and considerable confusion is often caused thereby, when the standard conditions are not specified.

In the following table the gross and nett calorific values are given of unit volume of the constituents present in any quantity in ordinary coal gas; for convenience, the values are given both in Cal. per cubic

<sup>1</sup> The Editor is indebted to the Controller of His Majesty's Stationery Office for permission to reproduce this table from Appendix G of the "Notification of the Gas Referees for the Year 1906."—C. A. K.

## Calorific Power of Gases.

Gas.	Calories per cubic metre.						B. Th. U. per cubic foot.											
	0° C. and 760 mm. dry.			15° C. and 760 mm. dry.			15° C. and 760 mm. moist.			32° F. and 30 in. dry.			60° F. and 30 in. dry.			60° F. and 30 in. moist.		
	Gross.	Nett.		Gross.	Nett.		Gross.	Nett.		Gross.	Nett.		Gross.	Nett.		Gross.	Nett.	
Hydrogen . . . . .	3056	2621		2897	2484		2848	2443		344	295		326	279		321	275	
Carbon monoxide . . . . .	3056	...		2897	...		2848	...		344	...		326	...		321	...	
Sulphuretted hydrogen . . . . .	6170	5745		5849	5446		5751	5355		693	645		657	612		646	602	
Methane . . . . .	9572	8699		9074	8246		8922	8108		1076	977		1020	927		1008	911	
Ethylene . . . . .	15063	14190		14279	13451		14041	13226		1692	1594		1605	1511		1578	1486	
Propylene . . . . .	22136	20832		20983	19747		20633	19417		2487	2341		2353	2219		2319	2132	
Benzene vapour . . . . .	33397	34093		33553	32318		32992	31777		3977	3831		3771	3631		3708	3570	

*Further deduction from nett values to be made if the sensible heat of the condensed water evolved by the cooling from 100° to 15° C. is to be allowed for.*

	Calories per cubic metre.			B. Th. U. per cubic foot.		
	0° C. and 760 mm. dry.	15° C. and 760 mm. dry.	15° C. and 760 mm. moist.	32° F. and 30 in. dry.	60° F. and 30 in. dry.	60° F. and 30 mm. moist.
For $H_2$ and $H_2S$ . . .	68	64.5	63	7.6	7.25	7.1
" $CH_4$ and $C_2H_4$ . . .	136	129	126	15.2	14.5	14.2
" $C_2H_6$ and $C_6H_6$ . . .	204	193.5	189	22.8	21.75	21.3

mètre, and B.Th.U. per cubic foot. Further, in each set, figures are given showing the values at (a)  $0^{\circ}$  C. and 760 mm., or  $32^{\circ}$  F. and 30 in. dry; (b)  $15^{\circ}$  C. and 760 mm., or  $60^{\circ}$  F. and 30 in. dry; and (c)  $15^{\circ}$  C. and 760 mm., or  $60^{\circ}$  F. and 30 in. moist.

The figures in the table are calculated from the observed calorific power of known weights of the various gases, and their specific gravities, Thomsen's values being employed except in the case of benzene vapour. The figures found for the latter by Thomsen, Berthelot, and Stohmann vary considerably, and as the latter approximates to the average of all the values obtained, it has been taken in preference to Thomsen's figure.

The figures given for the nett values in the table are obtained by deducting the latent heat of the steam produced (0.537 Cal. per c.c.) from the gross figures. In the experimental determination of calorific power with the calorimeter, it is customary to deduct the round figure of 0.6 Cal. for each cubic centimetre of condensed water; this includes the latent heat of the steam, and also, approximately, the sensible heat evolved to the calorimeter by the cooling of the condensed steam from  $100^{\circ}$  C. to atmospheric temperature. This last amount of heat, however, should not be deducted if the true thermodynamic nett value is to be ascertained, as it is evolved as heat in the flame and is available for development of flame temperature and of mechanical energy under normal conditions. An additional table is given, showing the further deductions which must be made from the nett values given in the first table, if it be desired to allow also for the sensible heat of the condensed steam.

### Calculation of the Calorific Power from the Analysis.

If the composition of the gas is known, its calorific power may be calculated from the values of the constituents given in the above table by multiplying the percentage of each constituent by its calorific power, and dividing the sum of the multiples by 100, as shown in the following example:—

	Per cent. by volume.		Gross Cal. Power at $60^{\circ}$ F. and 30 in. moist.		Multiple.
$\text{CO}_2$	1.2	×	nil	=	...
$\text{C}_n\text{H}_m$	3.4	×	2319	=	7885
$\text{O}_2$	0.3	×	nil	=	...
$\text{CO}$	6.8	×	321	=	2183
$\text{CH}_4$	32.9	×	1003	=	32999
$\text{H}_2$	49.2	×	321	=	15791
$\text{N}_2$	6.2	×	nil	=	...
					<hr/> 58858 ÷ 100 = 588.6

The calculated calorific power of such a sample of gas is, therefore, 588.6 B.Th.U. gross per cubic foot measured moist at  $60^{\circ}$  F. and 30 in.

The value thus obtained is, of course, subject to all the errors of analysis, and a further possibility of error arises from the uncertainty as to the exact composition of the heavy hydrocarbons,  $C_nH_m$ . It is customary to assume that the mixture has the same calorific power as propylene, as has been done above, but this can only be regarded as an approximation. Usually, however, in the case of coal gas, the analyses thus calculated agree to within 2 to 3 per cent. with the figures obtained by the calorimeter. With carburetted water gas, in which a much higher percentage of unsaturated hydrocarbons is present, the agreement is often much less satisfactory.

If the percentages of ethylene and benzene have been separately determined by any of the methods previously described, these figures are multiplied by their respective calorific powers, instead of employing the propylene values.

### The Direct Measurement of the Calorific Power.

In place of the indirect and tedious estimation of the calorific power by calculation from the complete analysis, this value is now almost always obtained by direct measurement.

The calorimeters in use, for estimations in which large volumes of gas are available, are all modifications of the calorimeter devised by Hartley<sup>1</sup> in 1882, in which the gas is burned at a constant rate in a chamber through which water is flowing also at a constant rate. From the volume of gas consumed and of water passed in a given time through the apparatus, and the average increase in the temperature of the water, the calorific power is readily calculated. The amount of water condensed from a given volume of gas also supplies a ready means of ascertaining the necessary deduction for the latent heat of water required to determine the nett calorific power.

Two instruments of this type, namely, the Junkers' and Boys' calorimeters, have already been described in the section on "Technical Gas Analysis" (Vol. I, p. 226), and the method of carrying out the tests fully discussed. The Simmance-Abady calorimeter<sup>2</sup> is also frequently employed. In its main outlines, this resembles the Junkers' instrument, but in place of the hot gases passing through tubes, traversed on the outside by water in the reverse direction, they travel downwards through a series of annular chambers separated by similar chambers up which the water flows. Both thermometers in this instrument are at the same level, and by their side is a manometer tube to show the pressure of the inlet water, which must be kept constant; a damper is provided at the waste gas exit, for the regulation of the

<sup>1</sup> *Report of Gas Section, Crystal Palace Exhibition*, vol. i., p. 25; *Trans. Gas Institute*, 1884, p. 123; *J. Gas Lighting*, 1884, 43, 1142.

<sup>2</sup> Made by Messrs A. Wright & Co., Westminster.

volume of air passing through the apparatus, and the condensed water flows to the bottom, and thence through a small exit drain into a measuring cylinder. The method of working and the calculation of the results are the same as with the Junkers' and Boys' instruments.

For accurate calorimetric determinations, it is, of course, obvious that the gas meter and thermometers must be correct, and that the gas and water supplies are properly governed so as to pass at a uniform rate. The measurement of the water may be made either by weighing or measuring; the latter is the more accurate method, owing to the fact that the water is measured warm, and therefore 1 c.c. weighs rather less than 1 g., but the error from this cause is slight. In addition, it is very important that the temperature of the inlet water should keep nearly uniform, and should not differ from that of the room by more than 2° or 3°.

Further, as the waste gases always pass away saturated with water, a small error in the gross value is introduced by variations in the amount of moisture in the air also taken through the apparatus. The gas, being measured through a wet meter, is always saturated, and if the air is also saturated, some of this moisture will be separated as liquid water in the calorimeter, owing to the contraction of the gases which occurs on combustion; its latent heat will thus be added to the heat evolved by the gas, and increase the gross value. If, on the other hand, the air is very dry, some of the steam formed by the combustion of the gas will be carried away uncondensed with the waste gases, and thus make the gross value rather too low. With the ordinary variations of atmospheric moisture in this country, however, the error from this source rarely exceeds 1 per cent.; the nett value is in any case unaffected, as the gross value and the deduction for condensed water are equally affected, so that the difference, which is the nett value, is not altered.<sup>1</sup>

When only small quantities of gas are available, other forms of calorimeter have been devised. Those of Fischer and Hempel have been mentioned (Vol. I., p. 236). In addition, the Simmance-Abady instrument, for small amounts of gas,<sup>2</sup> gives good results if previously calibrated with gas of known calorific power. A new still water calorimeter, which can be used with very small quantities of gas, has recently been described by J. H. Coste and B. R. James.<sup>3</sup>

<sup>1</sup> For further discussion of the various sources of error and their magnitude, cf. "Report of American Gas Association Calorimetry Committee," *J. Gas Lighting*, 1908, 104, 904; also J. H. Coste, *J. Soc. Chem. Ind.*, 1909, 28, 1231; Klumpp, *J. Gas Lighting*, 1910, 110, 823.

<sup>2</sup> Made by Messrs A. Wright & Co., Westminster.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1911, 30, 258.

## B. PHOTOMETRY

Although, as already pointed out, the illuminating power of coal gas no longer possesses its former primary importance, as showing its comparative value to consumers, its determination is still required, in view of the fact that a small proportion is even now used for illuminating purposes in flat flame burners. The chief reason for its determination, however, is that under existing statutory regulations, gas of a certain specified minimum illuminating power must be maintained by all statutory Gas Undertakings, the actual quality fixed varying considerably in different towns and districts.

In addition to the determination of the illuminating power of the gas due to the luminosity of the flame burning in the air, photometrical measurements are also required for many other purposes, such as the estimation of the illuminating power of gas when burned with a mantle in an incandescent burner, the relative amounts of light emitted by the various burners at different angles, and also of the actual illumination produced on the surfaces in both interior and outdoor lighting by these burners. To deal with these applications of photometry, which are equally necessary in all cases of artificial illumination, from whatever source of light, would require much more space than is available in the present work. The consideration of the subject will, therefore, be confined to the methods of determination of the mean spherical illuminating power of the gas when burnt with a luminous flame.

**Principles of Photometry.**—The chief principle involved in the determination of illuminating power is that when two surfaces, on which no other light is falling, are equally illuminated by two separate sources of light, the relative intensities of the two sources of light are proportional to the square of their distances from the surfaces they are respectively illuminating. Hence if A and B represent the illuminating power of the two sources of light, and  $a$  and  $b$  their respective distances from the illuminated surfaces when the latter are equally illuminated, then :—

$$A : B = a^2 : b^2.$$

If one of the sources of light has a known intensity, that of the other can, therefore, be readily calculated by measurement of the distances at which both produce equal illumination.

The essential parts of an apparatus for such photometric determinations are therefore :—(1) A standard source of light ; (2) a burner in which the gas can be burned under definite conditions ; (3) apparatus for accurately measuring the distances at which the standard and gas flame effect equal illumination.

**1. Standards of Light.**—Until the closing years of the nineteenth century, the only standard legally recognised in this country was the

standard sperm candle, the average light emitted by which was, and still is, taken as the unit of light, the illuminating value of the gas being expressed in terms of the number of such candles to which the light evolved by the gas is equal when burned at the rate of 5 cb. ft. per hour. The only legal definition of the standard candle is that contained in the London Gas Act, 1860, where these are defined as "sperm candles of six to the pound, each burning 120 grains per hour."

This standard has proved to be of a very unsatisfactory nature, but in spite of its disadvantages it was long before a more reliable and generally acceptable standard was found, the eventual solution of the problem, so far as Great Britain and Ireland was concerned, being due chiefly to the labours of A. Vernon Harcourt, the senior Metropolitan Gas Referee, who employed as standard the flame produced by air saturated with pentane vapour at the ordinary temperature. In his earlier standards, Harcourt prepared the mixture in a special gas holder, and burned the gas at such a rate as to give a light equal to one standard sperm candle; but in the apparatus finally adopted, the mixed air-pentane gas is produced automatically as required, and burned in such a manner as to give a light equal to 10 sperm candles.

The Harcourt 10-candle standard was first officially adopted for statutory tests in the Metropolis in 1898, and since then many other Gas Undertakings have obtained special powers to employ the lamp in place of candles. As, however, the general Act relating to Gas Undertakings (the Gas Works Clauses Act, 1871) remains in force, in which the use of candles is specified, all Undertakings which have not obtained such special clauses are still compelled to employ candles as the standard of light for all statutory tests.

For non-statutory tests, such as those for information purposes on the works, the Harcourt 10-candle standard is employed to a constantly increasing extent. For quick-reading, works' photometers,<sup>1</sup> however, the Methven screen and the Simmance-Abady 1-candle and 2-candle pentane standards are used in many cases.<sup>1</sup>

In Germany, the standard is the Hefner amyl acetate lamp, in which the flame is produced by pure amyl acetate, and in France the Carcel lamp is used for gas testing purposes, in which colza oil is burned. These two standards, together with the Harcourt 10-candle lamp, and candles will now be described in greater detail.

(a) *Sperm Candles.* In the manufacture of these, pure spermaceti, having a melting point of 109° F., is employed, to which a sufficient quantity of bleached beeswax of melting point 140° F. is added to "break the grain" of the spermaceti. In testing, the Gas Works

<sup>1</sup> Descriptions of these, and of many other proposed forms of standard may be found in Abady's *Gas Analysts Manual*, 1902.

Claudes Act specifies the use of two candles, the usual practice being to divide a single candle in the centre, cutting away half an inch of sperm from each freshly cut end, care being taken not to damage the wick. The candles are placed in a suitable balance, in order that their exact rate of consumption may be ascertained, as this rarely takes place at the specified rate of 120 grains per hour, and a proportional correction is made for deviation from the standard rate. Before making the actual test, the candles must have been burning for at least ten minutes to attain normal conditions, indicated by the fact that the shallow cup formed by the action of the flame is "semi-dry," and that each wick shows a uniform bend and has a glowing tip. If these conditions are not fulfilled after some time, the candles should be rejected. When testing, the planes of the curved portions of the wicks should be placed at right angles to each other.

(b) *The Harcourt 10-candle Pentane Lamp.*

This lamp is illustrated in Fig. 108. The saturator A is filled two-thirds full with pentane, the level of which is never allowed to fall below a height of  $\frac{1}{8}$ th in. above the bottom of the glass window shown. Air is admitted by the cock  $S_1$ , and travels in a zigzag path over the surface of the pentane, thus becoming saturated with the vapour, and therefore heavier than air, in consequence of which, on opening the stopcock  $S_2$ , it falls down through the wide rubber tube to the Argand burner B, which has an annular steatite tip, perforated by thirty holes not less than 1.25 or more than 1.5 mm. in diameter. The flame is drawn into form by the brass chimney C, 30 mm. in internal diameter, the lower end of which is fixed exactly 47 mm. above the top of the steatite ring when the burner is cold, a cylindrical boxwood gauge, 47 mm. long and 32 mm. in diameter, being provided to set this accurately. Outside the chimney C is fixed a larger concentric chimney, D, the annular space between the two communicating with the interior of the steatite ring through the connecting box and bracket E, on which the burner is supported; the centre of the flame is thus supplied with warm air, heated by the flame, through the chimney C.

A mica window marked with a cross bar is placed in the lower end of the chimney C, and the gas supply to the flame is regulated so that

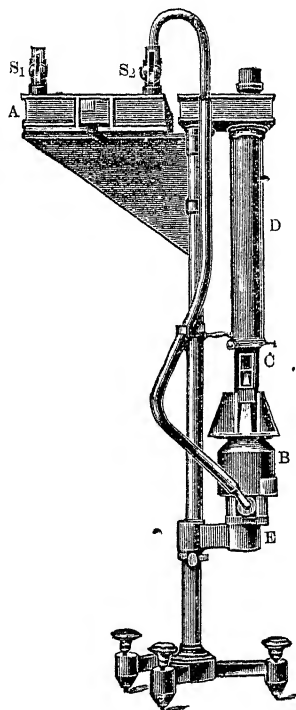


FIG. 108.



the average tip of the flame, as seen through this window, is half-way between the cross bar and the bottom of the window; the regulation is effected by means of the stopcock  $S_2$ . The regulation may be made more conveniently by opening  $S_2$  sufficiently to give rather too high a flame, and effecting the fine adjustment by a damper covering the inlet air-cock  $S_1$ , worked from the operator's seat by means of a fine cord and pulleys.

The lamp must be burned for fifteen minutes before making a test, the final regulation of the height of the flame being made just previous to commencing the test. To facilitate this, the chimney C is so turned that it is visible from the operator's seat, but at the same time in such a position that the light from it cannot fall on the disc box or photoped of the photometer. (The position of the mica window shown in the figure for convenience of illustration, would not be permissible in testing, as the light from it would then fall on the disc.) Owing to the fact that the top of the flame is screened off, the height of the flame may vary  $\frac{1}{4}$  in. either way from the specified height without greatly affecting the light emitted by the screened portion. The flame is surrounded by a conical screen having an opening on one side which is turned in such a manner as to allow the whole of the light from the flame below the chimney to fall on the disc box or photoped.

The pentane employed (which consists chiefly of isopentane) is obtained by the fractional distillation of light American petroleum, and should have at  $15^\circ$  C. a specific gravity of not less than 0.6235, or more than 0.626, compared with water at  $4^\circ$ , and a vapour density of between 36 and 38 compared with hydrogen. Hydrocarbons of other groups, *e.g.*, olefines and benzenes, must be absent.<sup>1</sup>

The Harcourt 10-candle pentane standard, like all other flame standards, is not absolutely constant, as the light given out is affected by the conditions of the atmosphere in which it burns, variations in the percentages of oxygen, carbon dioxide and moisture, and the atmospheric pressure all having an effect. No direct data are available as to the effect of variations in the oxygen content of the air, but the effect of the other three factors has been determined at the National Physical Laboratory.<sup>2</sup> The standard conditions under which the light of the lamp is 10 candles are taken as the normal barometer pressure of 760 mm., and a moisture content of 8 litres of water vapour per cubic metre of dry air, as determined by a ventilated hygrometer of the Assmann type. The ordinary variations in carbon dioxide are without material influence, but the illuminating power increases 0.66 per cent. with each fall of 1 litre of water vapour per cubic metre of dry air, and 0.8

<sup>1</sup> For further details and dimensions, *cf.* the *Notification of the Gas Referees*, 1906, published by Wyman & Sons, Fetter Lane, London, E.C.

<sup>2</sup> C. C. Paterson, *Proc. Phys. Soc.*, 1909, 21, 867.

per cent. for each increase of 10 mm. in barometric pressure, the correct amount of light under standard conditions being found by the formula :—

$$10 + 0.066(8 - \epsilon) - 0.008(760 - b),$$

where  $\epsilon$  = number of litres of water vapour per cubic metre of dry air as found by a ventilated hygrometer, and  $b$  is the height of the barometer.<sup>1</sup>

In gas testing, however, such correction is not made, inasmuch as both the standard and the light tested are flames, and it is assumed that in that case both are equally affected by the alteration in conditions, so that the comparison of the two would be unaltered. This assumption is doubtless true in so far that the light given by the flames is altered in the same direction, but it is most probable that they are affected to a varying extent, and that the comparison is also to some extent affected; there are, however, no data yet available by which any correction in this respect can be made.

(c) *The Hefner Lamp.* This standard, which is universally employed in Germany, and also to a considerable extent in other countries, was devised by Hefner v. Alteneck.<sup>2</sup> The standard light unit is defined as the illuminating power of a flame of pure amyl acetate, burning freely in a still atmosphere, from the top of a solid circular wick contained in a nickel-silver tube of 8.0 mm. internal and 8.3 mm. external diameter, which projects 25 mm. above the amyl acetate reservoir with which it is connected. The flame is regulated to a height of 40 mm. above the top of the tube containing the wick, at least ten minutes being allowed for the lamp to attain normal conditions of burning before making a test. This unit is known as the "Hefner," and has a value equal to 0.9 candle (*cf.* also p. 703).

The construction of the lamp is readily seen from Figs. 109 and 110. The wick must completely fill the burner tube and be of fairly loose texture, its upper end being almost level with the top of the nickel silver tube, and the lower end dipping into the amyl acetate in the reservoir. The height of the flame is regulated by the worm and wheel adjustment  $\alpha$ , its exact height being determined by observation through the eye-piece K. The amyl acetate employed must be of a high degree of purity.

The light emitted by this standard is also affected by variations in the atmospheric pressure and moisture; the former factor has, however, a much smaller influence than with the Pentane lamp. According to the investigations of Liebethal, carried out at the Berlin Reichsanstalt, in which normal conditions are taken as 760 mm. pressure and 8.8 litres of moisture per cubic metre of dry air, the corrections for variations in these respects are given by the formula :—

$$\text{Actual light in Hefners} = 1 + 0.055(8.8 - \epsilon) - 0.001(760 - b),$$

<sup>1</sup> Correction tables for the ordinary variations of atmospheric pressure and moisture have been published by Messrs A. Wright & Co., Westminster.

<sup>2</sup> *J. Gasbeleucht.*, 1884, 27, 766.

where  $e$  equals number of litres of water vapour per cubic metre of dry air, and  $b$  the height of the barometer.

This lamp has proved a valuable standard. The chief objection to it is that the flame has a reddish tinge differing materially from that of the flames with which it is compared. Many observers also

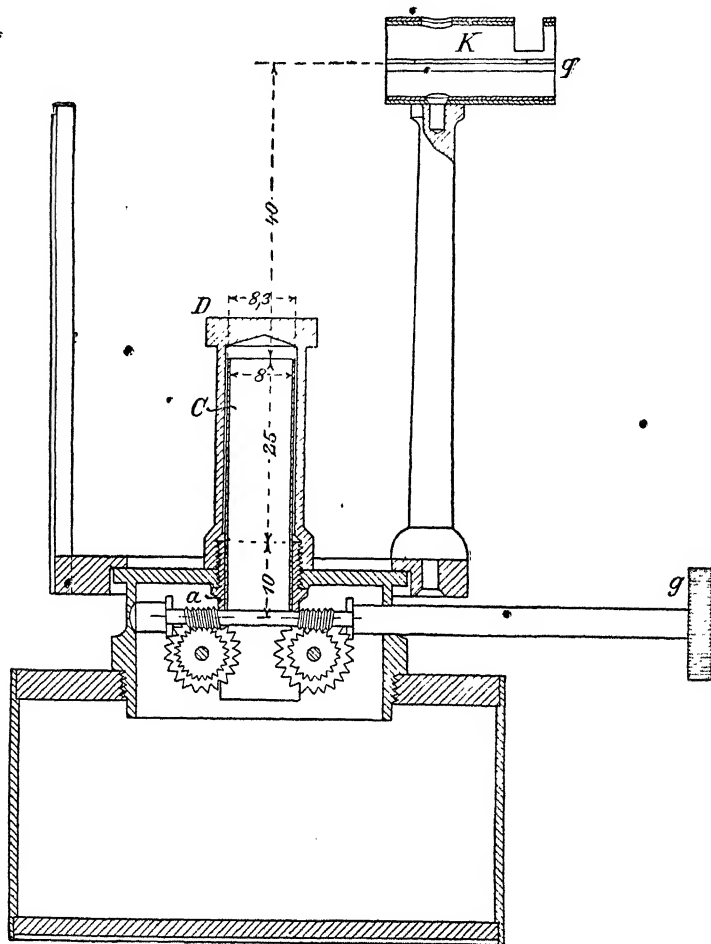


FIG. 109.

prefer to have a standard of higher illuminating power, and one more nearly equal to that of the light tested.

(d) *The Carcel Lamp.* This lamp, used chiefly in France, is a colza oil lamp, with an annular wick and burner, the oil being forced up into the wick by a small clockwork pump. The height of the wick should be regulated to 8 to 10 mm., the shoulder of the chimney being about 7 mm. above the wick, and the flame 38 mm. in length. The normal

consumption of oil is taken as 42 g. per hour, the exact rate of burning being ascertained by weighing in a similar manner to that employed with candles, and the light evolved calculated as proportional to the consumption. The limits of variation allowed are from 38 to 46 g. per hour, but it is preferable to keep this within the limits of 40 and 44 g.

This standard is much inferior in constancy to either the Pentane or Hefner standards, and in this respect more nearly resembles candles.

*Comparison of Standards and*

*Units.* During the past few years a number of comparisons of the different standards have been made by the National Physical Laboratory,<sup>1</sup> the Bureau of Standards, Washington, the Physikalisch-Technische Reichsanstalt, Berlin, and the Laboratoire Central d'Electricité, Paris, as a result of

which the British, American, and French Institutions have agreed on the relations to be accepted between the various units and standards.

The British unit remains the candle, this being one-tenth of the light emitted by the Harcourt 10-candle pentane lamp, burning under normal conditions. The French unit, the "bougie decimale," is the twentieth part of the Violle unit (the light emitted by 1 sq. cm. of platinum at its point of solidification), equal to 0.104 Carcel, and is found to be practically identical with the British candle. The American candle is 1.6 per cent. higher than this unit, and from April 1909 has been reduced to bring it into agreement with the British and French units, and the French, British, and American Institutions have agreed to the designation of this unit as the International candle. The relation of the standards and units is taken as follows:—

1 International candle	= 1 pentane candle
	= 1 bougie decimale
	= 1 American candle (from April 1909)
	= 1.11 Hefner unit
	= 0.104 Carcel
1 Hefner unit	= 0.90 International candle
1 Carcel	= 9.61 " "

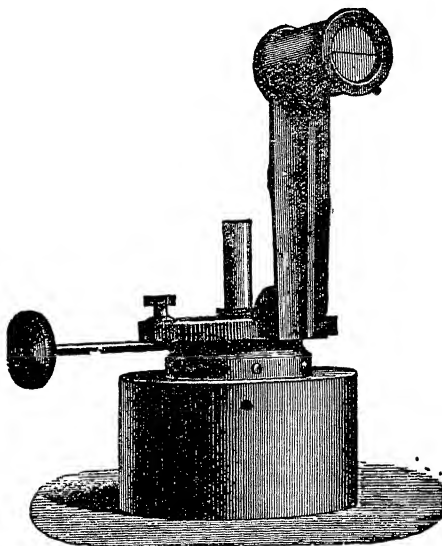


FIG. 110.

<sup>1</sup> Cf. *J. Soc. Chem. Ind.*, 1909, 28, 592.

The German Institution, however, has not accepted the above unit, and has preferred to retain the Hefner as the unit of light.

**2. Standard Burners for the Gas.**—It has already been pointed out that the illuminating power of any gas depends very materially upon the construction of the burner and the rate at which the gas is burned, and it is, therefore, necessary to specify the conditions which must be adhered to in this respect when making tests. Unfortunately no generally accepted conditions have been agreed upon in the past, with the result that widely different methods are adopted in different localities, and often prevent any true comparison being made between the figures obtained. Even when the method at first sight appears to be the same, this may not be the case in reality, as the same rate of consumption and the same burner do not necessarily give comparable results with gases of considerably different illuminating power, or with gas of the same illuminating power but widely different composition, as in the case of coal gas and carburetted water gas of about the same quality.

This unfortunate state of things has brought about considerable controversy, more especially in connection with the determination of illuminating power, as between the Gas Undertaking and the controlling authority, and also in relation to the proper method of ascertaining the true relative illuminating power of gases in connection with the manufacturing process. In the latter case, the method of burning the gas should be such as to give, with all qualities of gas tested, a figure which represents approximately the "mixing value" of such gas—*i.e.*, the proportional effect the gas would have on the illuminating power when mixed with other gases. Thus, for example, a gas testing 13 candles when mixed with an equal volume of gas testing 19 candles would be expected to give a mixture of 16 candle power, whereas by some of the methods of testing adopted, the mixture thus obtained is found to have an illuminating power of from 17 to 17.5 candles instead of the calculated 16 candles. The reason for this difference is that the conditions of burning adopted are suitable for the development of the full illuminating power of 17 candle gas, but are quite unsuited to gas of much higher or much lower quality, and in both cases yield a result much lower than the gas is capable of giving under more suitable conditions. In the case of statutory tests as between the Undertaking and controlling authority, the question of the true relative illuminating power is of less importance to the latter, who are mainly concerned in seeing that a certain minimum specified standard of illuminating power is maintained, but the adoption of a different method for such statutory tests from that employed for works purposes is very disadvantageous, and increases the difficulties of those engaged in the industry.

The number of different types of burner and conditions of testing in the various Undertakings throughout the country is very considerable, but only those which are now most widely employed will be considered, namely:—the London No. 1 Argand, and the Metropolitan No. 2 Argand, together with two types of flat flame burner which are employed in certain cases.

*The London No. 1 Argand.* In the London Gas Act of 1868, the duty of prescribing the methods to be adopted in testing London gas was placed upon a Board of Referees (the "Metropolitan Gas Referees") appointed by the Board of Trade, with the proviso that "the burner for testing illuminating power shall be such as is most suitable for obtaining from the gas the greatest amount of light, and be practicable for use by the consumer." In accordance with this principle, the Referees prescribed the use of the Argand burner devised by Sugg, known as the London No. 1 Argand. This burner is illustrated in Fig. 111; A are the gas supply pipes, B the gallery for supporting the chimney, C a cone to regulate the air supply to the outside of the flame, D an annular steatite chamber, forming the burner proper, and E the chimney. The chief dimensions of the burner are as follows:—

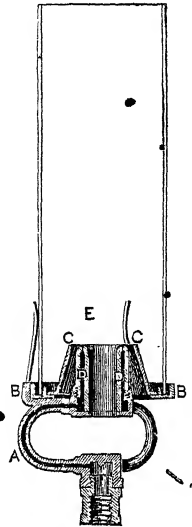


FIG. 111.

Diameter of supply pipe . . . . .	0.08 in.
External diameter of annular steatite chamber . . . . .	0.84 "
Internal " " " " . . . . .	0.48 "
Number of holes . . . . .	24 "
Diameter " " " " . . . . .	0.045 "
Internal diameter of cone at bottom . . . . .	1.5 "
" " " " top . . . . .	1.08 "
Height of upper surface of cone and of steatite chamber above floor of gallery . . . . .	0.75 "
Height of chimney . . . . .	6 "
Internal diameter of chimney . . . . .	1.875 "

In this burner, according to the then universal practice, the gas was burned at the constant rate of 5 cb. ft. per hour, and the dimensions were so arranged by Sugg that the amount of air admitted around the flame was suitable for the development of the greatest amount of light with that burner, when gas of the illuminating power (16 candles) and composition produced at that time in London was burned at the 5 cb. ft. rate. Under these conditions satisfactory results were obtained.

After the burner was officially recognised in London, it was also adopted in the case of many other Undertakings, often quite irrespective of its suitability for the quality of gas supplied, and it was soon

realised that with gases of below 16 candles and above 18 candles relatively low results were obtained with the burner when burning the gas at the rate of 5 cb. ft. per hour, as in the first case too much air entered the burner and minimised the separation of solid carbon particles in the flame, and in the latter case too little air was present, resulting in the formation of a dull and smoky flame. Further, the altered methods of manufacture resulted in the production of gas which for the same illuminating power required less air for its combustion, so that even with 16 candle gas the flame was over aerated, and the admixture of carburetted water gas had the same effect to a still greater extent. The lower the illuminating power the greater is the depreciation caused by admission of excess of air to the flame.

As early as 1870, it was shown by Hunt<sup>1</sup> that more nearly relative results for the illuminating power might be obtained with coal gas of widely different illuminating power with the No. 1 Argand by abandoning the constant rate of consumption of the gas, and burning the latter at such a rate that the chimney is nearly full of flame and just short of the smoking point, the illuminating power for the 5 cb. ft. rate being calculated by proportion from the observed rate of consumption. This method of testing was in many cases adopted in determining illuminating power for works purposes. For statutory purposes, however, the fixed 5 cb. ft. rate was universally retained for many years, although in some cases modified Argand burners were employed, in which the amount of air entering was checked to some extent, either by using a smaller chimney, or by restricting the passages through which the air was admitted.

The general adoption of the incandescent burner, with the consequent tendency to reduction of the illuminating power of the gas supplied, rendered the question more acute, but in the case of statutory tests agreement as to the introduction of a modified method of testing was rendered much more difficult, inasmuch as the matter could not be decided on purely photometric grounds, the question of altering the method of testing being closely involved with others, such as the alteration of the quality to be actually supplied, and financial adjustments. Eventually, however, after a controversy extending over several years, matters were settled, so far as London was concerned, by the London Gas Act, 1905, which modified the burner clause of the 1868 Act, referred to above, as follows:—"The burner prescribed shall be of such a pattern (not being an incandescent or similar burner) as shall be practicable for use by the consumer; the burner and the chimney (if any) shall be the most suitable for obtaining, and in making the test shall be so used as to obtain from the gas when burned at the rate of 5 cb. ft. per hour, the greatest amount of light."

<sup>1</sup> *J. Gas Lighting*, 1870, 19, 158.





Number of holes in burner	.	.	.	.	24
Diameter "	"	"	"	"	0.06 in.
Distance from top of steatite to top of outer cone	.	.	.	.	0.05 "
Centre peg	.	.	.	.	$1.355 \times 0.122$ "
Adjustable damper plate diameter	.	.	.	.	1.668 "
" " depth	.	.	.	.	0.375 "
Chimney height	.	.	.	.	6 "
Chimney internal diameter	.	.	.	.	0.625 "

The essential point of the burner is the adjustable damper plate, which controls the air supply passing to the interior of the Argand flame, and also that portion of the external supply passing up between the inner cone and the steatite annulus; this damper, previous to testing, and after adjusting the rate of consumption to 5 cb. ft. per hour, is screwed up until the air supply is such that the flame is just short of the smoking point, and the illuminating power of the gas is taken under these conditions.

In this manner, gases of widely different illuminating power and composition, but not exceeding 20 candles, can be tested with fairly accurate comparative results, and the method is equally applicable for both statutory and works tests, whether the gas is coal gas, carburetted water gas, or a mixture of the two. The results represent with sufficient nearness the true "mixing value" of all these gases. Since its prescription in London in 1905, it has been adopted by numerous other Undertakings throughout the country, and is also specified in the parliamentary "Model Clauses" for new Undertakings. Its use will probably eventually become universal in this country for illuminating power tests with a luminous flame, so far as these are not altogether superseded by calorific power tests.

*Standard Flat Flame Burners.* In cases where it is desired to determine the illuminating power of the gas burned in a flat flame either of two different burners may be employed, according as the gas is over or under about 20 candle power. For high quality gas, a steatite batwing burner (known as No. 7) is used, consisting of a hollow cylindrical stem, the top of which has a slot of uniform width. The dimensions are as follows:—

External diameter of steatite top	.	.	.	.	0.31 in.
Internal " "	.	.	.	.	0.17 "
Width of slot	.	.	.	.	0.02 "
Depth " "	.	.	.	.	0.15 "

For low quality gas, the burner specified by the Metropolitan Gas Referees is that manufactured by Messrs Bray & Co., Ltd., and stamped  $\frac{G}{L}$  5 ft.  $\frac{15}{10}$ . It consists of a brass tube nearly  $\frac{7}{16}$  in. in diameter, and  $\frac{3}{4}$  in. long, with a tapered and screwed end in which are secured

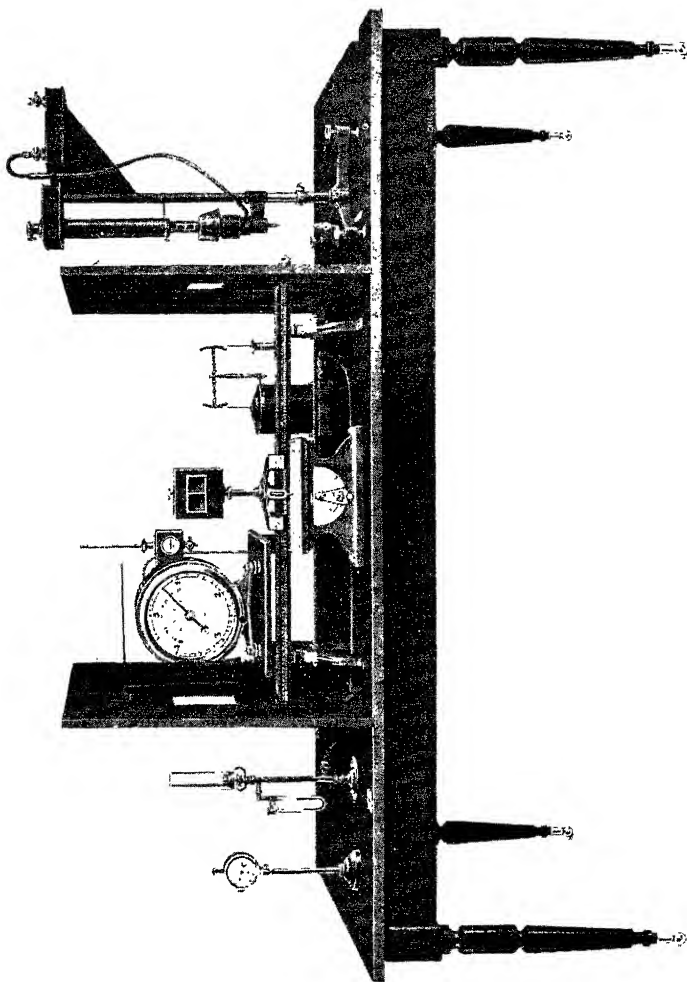


FIG. 113.



the following parts, through which the gas passes in order:—A steatite disc with a round hole in the middle between 0.055 and 0.060 in. in diameter; a diaphragm consisting of three thicknesses of gauze; a second similar diaphragm separated by a space from the first; a steatite batwing burner with a semicircular slit and having an external diameter at the base of between 0.32 and 0.33 in. and a width less than 0.029 and greater than 0.027 in. With both burners the gas is burned at the rate of 5 cb. ft. per hour.

**3. Photometric Apparatus.**—Two types of photometer are now in common use, namely, the bar-photometer and the table-photometer. The former and older form is most frequently employed, and can be used for gases of widely different quality. The table-photometer, due to the Metropolitan Gas Referees, was more especially devised for determining the illuminating power of the gas sent out to the district of supply by a Gas Undertaking; it is less suitable for the testing of gases of widely different illuminating power.

*The Bar-Photometer.* The standard of light and the specified gas burner are fixed at the opposite ends of a graduated bar, in such a manner that the bottom of each flame is the same height above the table, the exact horizontal distance between the centres of the two flames being generally fixed at 60 ins. The apparatus is provided with the necessary gas meter, governor, and adjusting cock for regulating the rate of consumption and maintaining it constant, and also with a stop-clock or watch for timing the meter and also the sperm consumption of the candles, when these are used. In addition, suitable screens are provided to prevent the light from the flames, other than that coming from the disc box, reaching the eye of the observer, and also to protect the flames from draughts. Fig. 113 illustrates a form of bar-photometer in frequent use, which shows the arrangement of the apparatus.

In order to determine the distances at which the two lights effect equal illumination, the Bunsen disc is most commonly employed in this country. This consists of a piece of white paper, which, with the exception of a circular spot in the centre about 1 in. in diameter, is made translucent by painting with a solution of spermaceti in benzene. This paper is placed in a suitable box, the interior of which is blackened, and fixed in it in such a manner that the plane of the paper is vertical and at right angles to the direction of the bar. The box itself is fixed on a carriage which can be moved along the bar in either direction, and at such a height that the centre of the disc is in line with the central axis of both flames, and the same height as the bottom of the burners. In this way one side of the disc is illuminated by the light standard and the other by the gas flame, and so long as the illumination is unequal the unpainted spot in the centre appears quite distinct, and

brighter than the painted portion on the more strongly lighted side. By means of mirrors placed at the back of the disc box, the observer is enabled to view both sides of the disc simultaneously, and by moving the disc carriage along the bar can find the point at which the unpainted spot nearly disappears, and especially the position at which the boundary line between the painted and unpainted portions appears to be exactly the same on both sides; this is taken as the point of equal illumination. The exact distances of the disc from each source of light are then read off on the bar, and the relative illuminating power of the two lights calculated from the square of the distances observed; usually, however, the bar is so graduated that the relative illuminating power is read off directly from the graduations.

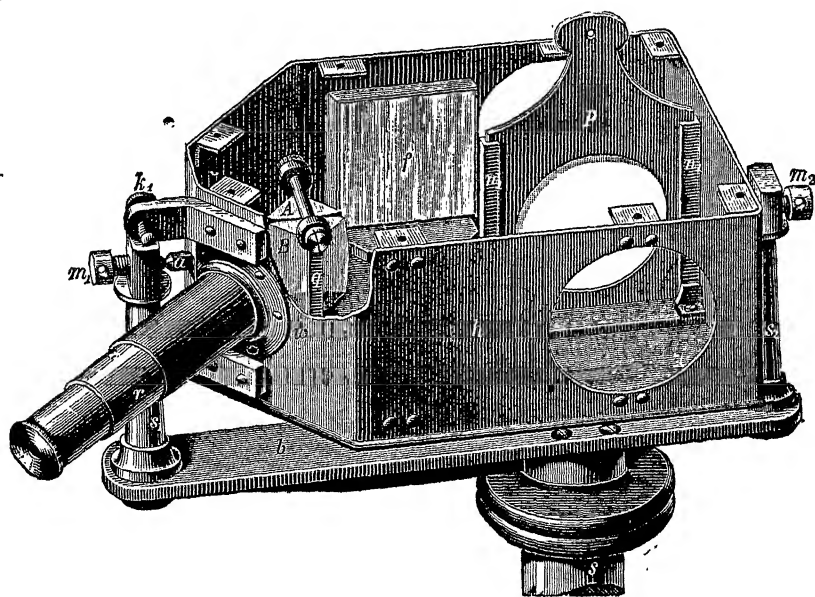


FIG. 114.

The delicacy of the discs varies considerably, some being found to be "soft," *i.e.*, the unpainted spot disappears completely on equal illumination, and no sharp determination of this point is possible. Others are found "hard," *i.e.*, the spot does not disappear sufficiently at the point of equal illumination, and in this case also a sharp reading is difficult to obtain. "Soft" discs cannot be improved, but "hard" discs may be softened to any desired point by very gentle warming; the exact degree of softness found most suitable varies considerably with different observers. Further, owing to differences in the two surfaces, the point found for equal illumination often varies if the surfaces are reversed, and the disc should be, therefore, so arranged that

it can be reversed, half the readings being taken with one position and the other half after reversing the disc. If any great difference is found on reversing, the disc should be rejected.

Another form of photometer head frequently employed in place of that of Bunsen, especially in Germany, is the *Lummer-Brodhun disc box* (Figs. 114 and 115). This consists of the metal box  $h$  (Fig. 114), in which a completely opaque white surface,  $p$ , is illuminated from both sides by the sources of light  $L_I$  and  $L_{II}$  (Fig. 115). The light falling on each side is reflected by the plane mirrors  $f$  and  $f_1$  to the glass prisms A and B respectively; the former is a right-angled prism, the surface opposite the right angle being cylindrical, but having a small surface,  $in$ , ground flat and closely pressed against the entirely flat surface,  $ow$ , of the prism B. The light from  $L_{II}$ , reflected from the right-hand side of the white disc  $p$  by the mirror  $f_1$ , illuminates the whole of the surface  $oi$  and  $nw$  of the prism B, but the light falling on the portion  $in$

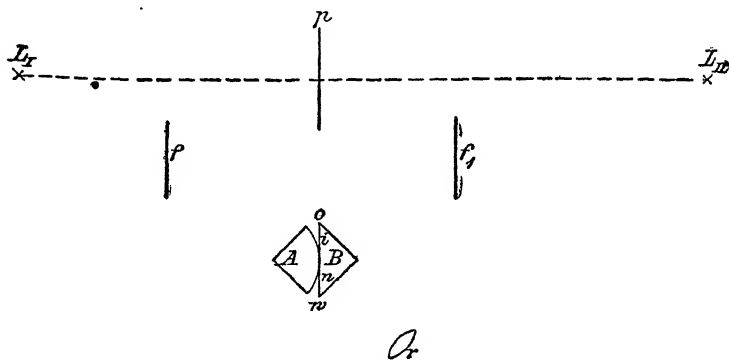


FIG. 115.

passes through the prism A, only the light from the surfaces  $oi$  and  $nw$  being reflected to the eye of the observer at  $r$ . If, therefore, no light is coming from  $L_{II}$ , the field of light observed through the eyepiece appears that of a lighted surface with a dark circle in the centre. If, on the other hand, light only comes from  $L_I$  by reflection from  $p$ , and the mirror  $f$ , only the surface  $in$  is illuminated, and appears to the observer as a bright central spot in a dark ground. If light is coming from both sources, the centre spot and the field are both illuminated, and if the illumination of both surfaces of  $p$  is equal, the central spot disappears and a uniform field of light is obtained.

The disc box is mounted on a carriage and moved to and fro along the bar till the point of equal illumination is found, just as with the Bunsen disc; in this case also, to avoid errors from inequality of the two surfaces of the disc  $p$ , this is made reversible and an equal number of readings are made in each position of the disc.

Both forms of disc suffer from the objection that the point of equal illumination is less readily ascertained when the colours of the two flames tested are materially different. With ordinary luminous gas flames, the extent of this error is not great to a practised observer, but in other cases, such as in the testing of incandescent burners, it is much more serious. For such tests, the *Sirrance-Abady flicker photometer head*<sup>1</sup> is largely employed. In this apparatus, reflections of each source of light are alternately transmitted to the observer in rapid succession by means of a specially arranged rotating disc, actuated by clockwork; so long as the light from each source is unequal a flickering effect is noticed, but this ceases as soon as equality of illumination is obtained, irrespective of the colours of the sources of light.

*Procedure in Testing with the Bar-Photometer.* The photometer is placed in a room capable of being completely darkened, and preferably having the walls and ceiling painted dead black to avoid reflection. The room should be free from draughts, but at the same time thoroughly well ventilated; it should be maintained at a temperature not below 15°, and as little above this temperature as practicable. Imperfect ventilation and a low temperature very materially influence the results, and give rise to very considerable errors, usually in the direction of making the results too low, especially when the 10-candle pentane lamp is employed; with candles the error may be in either direction.

The gas to be examined and the standard of light must be allowed to burn for at least ten to fifteen minutes before testing, in order to allow normal conditions of burning to be ascertained, more than this time being often necessary with candles. In the meantime the gas consumption of the burner is regulated to the desired rate. If the No. 2 Metropolitan Argand is being used, the rate of consumption is, as already mentioned, 5 cb. ft. per hour; but according to the instructions of the Gas Referees, a variation of 2 per cent. either way is permitted, due proportional correction being made in the calculations. Previous to testing, the damper of this burner must be screwed up until the flame in the chimney is just below the smoking point.

Normal conditions being obtained, the usual procedure, where candles are employed, is as follows:—The two candles, prepared as described on p. 699, and burning in the candle balance, are nearly counterpoised by shot, and when, on further burning, the pointer of the balance passes the zero point, the stop-clock or watch is started from zero, the reading of the meter noted, and a 40-grain weight placed on the balance pan beneath the candles. Readings of the disc are taken at the commencement of each minute, the disc being reversed after the

<sup>1</sup> *Proc. Phys. Soc.*, 1903-5, 19, 39.

fifth reading; at the ninth minute the reading of the meter is observed and, after taking the tenth reading, the candle balance is watched, and the clock stopped as the pointer passes the zero mark; the time recorded shows the time required by the two candles to burn 40 grains. If each burned at the standard rate of 120 grains per hour, this would be exactly ten minutes; it is assumed that the actual amount of light emitted by the candles is proportional to the rate of burning, so that if  $x$  is the number of minutes and seconds required for the burning of 40 grains, the light given by the two candles is  $\frac{2 \times 10}{x}$ . If, however, the candles burn at a greater rate than 42 grains or at a less rate than 38 grains in ten minutes (or, which comes to almost the same thing, if the time required to burn 40 grains is less than 9.5 minutes or greater than 10.5 minutes), this proportional correction does not hold good, and the test should be rejected.

The calculation of the illuminating power of the gas for 5 cb. ft. of gas, measured moist at 60° F. and 30 in. pressure, is as follows:—If the average readings of the disc carriage, using two candles, is 8.2, the time of burning of 40 grains sperm 10 min. 12 sec. (10.2 min.), the rate of gas consumption 5.05 cb. ft. per hour at 64° F. and 29.6 in. pressure, the corrected illuminating power is:—

$$\frac{2 \times 8.2 \times 10 \times 5.0}{5.05 \times 10.2 \times 0.976} = 16.31 \text{ candles,}$$

0.976 being the tabular number for correcting the volume of gas at 64° F. and 29.6 in. to that of moist gas at 60° F. and 30 in. as given in the table on p. 690.

When the pentane standard is employed, it is unnecessary to make so many observations as in the case of candles, as the light emitted remains practically constant throughout; in this case four readings are sufficient, the disc being reversed after two observations have been made. The rate of gas consumption is ascertained by observation of the time taken for two complete revolutions of the meter, which passes  $\frac{1}{12}$ th of a cb. ft. per revolution, and at the rate of 5 cb. ft. per hour requires 120 seconds for two revolutions, the exact rate of consumption being therefore  $\frac{5 \times 120}{s}$ , where  $s$  is the number of seconds observed. If  $s$  is 119 seconds, the average of the readings 15.82, the gas temperature 65° F., and the pressure 30.25 (tabular number = 0.996), the corrected illuminating power is:—

$$\frac{15.82 \times 119}{120 \times 0.996} = 15.75 \text{ candles.}$$

*The Table Photometer.* In this form of photometer, the standard of



light and the gas burner are so arranged on a table that the light from each burner passes through an oblong hole in a screen on to a sheet of translucent white paper, free from water marks, thus illuminating two adjacent portions of the paper which just touch each other without overlapping. The observer, from a position on the opposite side of the paper from the sources of light, is able to alter the conditions of the gas burner, either by varying the rate of consumption or by increasing or decreasing its distance from the screen, until both of the lighted portions of the paper appear equally illuminated.

The general arrangement of this photometer, as now adopted by the Gas Referees, is shown diagrammatically in Fig. 116, and is fully described with all dimensions in the *Gas Referees' Notification*.<sup>1</sup> The 10-candle pentane standard is fixed with the centre of the flame exactly 1000 mm. from the centre line of the surface of the translucent paper in the photoped place at the head of the table, the gas burner, in the present form of the photometer, being placed on a sliding carriage, movable along the dotted lines shown, the line of movement being such that the angle of incidence of the light from the burner at the centre line of the translucent paper is exactly equal to that of the light from the pentane burner at the same point. Suitable screens are provided to protect the eyes of the operator from direct rays of light from the flames; two mirrors are also employed, of which No. 1 allows the operator to observe the height of the flame of the pentane standard from his position at the head of the table, and No. 2 reflects light from the gas burner on to the face of the gas meter.

The gas enters the meter and passes thence through the governor to the regulating cock at the head of the table, and then to the gas burner. Both standard and gas burner must be allowed to burn fifteen minutes before making a test, the gas consumption being regulated in the meantime as described for the bar-photometer. The requirements as to temperature and ventilation mentioned for the latter instrument apply equally to the table photometer.

In the form of table photometer originally adopted, equality of illumination was obtained by varying the consumption of the gas with the regulating cock till equality of illumination was obtained, the gas burner being placed with its centre 1269 mm. from the photoped, so that when equal illumination obtained, the light given by the burner was 16 candles, the illuminating power for the 5 cb. ft. rate being found by proportion from the observed consumption. A modification of the photometer employed to make it more suitable for works' purposes and especially for making tests of carburetted water gas,

<sup>1</sup> Published by Wyman & Sons, Fetter Lane, London, E.C.

consisted in providing a number of sockets for the gas burner, placed at such distances from the photoped that, when equality of illumination was attained, the light given by the burner was 14, 15, 16, 17, 18, 19, or 20 candles, as desired.

The adoption of the Metropolitan Argand burner No. 2, in which

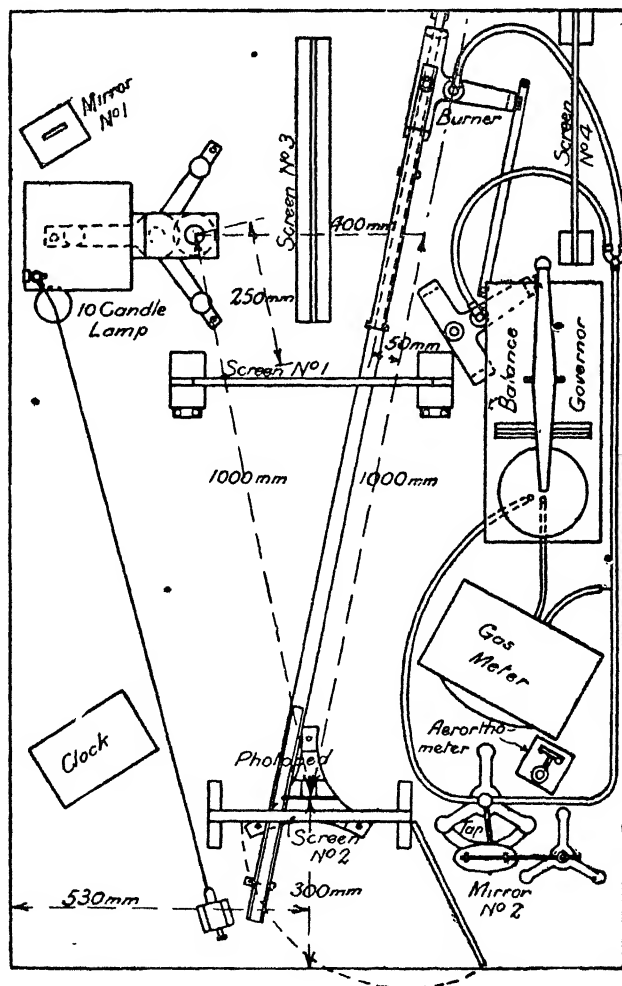


FIG. 116.

the gas consumption must be maintained at nearly 5 cb. ft. per hour, made it impossible to retain the above method of obtaining equality of illumination on the photoped, and this plan was, therefore, abandoned by the Gas Referees, in favour of placing the gas burner on a movable carriage as described above. This is actuated by the operator by

means of a long rod attached to the carriage, and reaching to the head of the table, and is furnished with a pointer working over a scale which is graduated so as to read off the actual illuminating power directly. This method of operation is, however, open to the objection that the flame of the burning gas, and especially that of the No. 2 Argand when the damper is adjusted, is very sensitive to any movement.

In making a test by this method, after uniform conditions have been attained and the gas supply adjusted to within 2 per cent. of the 5 cb. ft. rate, the damper of the No. 2 burner (when employed) is screwed up until the flame is just short of the smoking point, and four readings taken by pushing the connecting rod to the burner to and fro until the illumination of the two lighted surfaces in the photoped is judged to be equal, and the average of the four readings taken. The temperature of the gas and height of the barometer are noted, and the exact rate of consumption determined by observation of the number of seconds taken for two complete revolutions of the gas meter ( $\frac{1}{2}$ th cb. ft.), the calculations being exactly the same as those given above for the bar-photometer when using the pentane standard.

In all photometrical tests, it is, of course, essential for accuracy that the gas meter and stop-clock should be correct, and that the specified distances should be exactly maintained; all these points must be checked periodically and adjusted if incorrect. The meter is calibrated by means of a standard  $\frac{1}{2}$ th cb. ft. measure, and adjusted to correct reading by varying the water level in the meter. Suitable measuring rods are provided to check the distances of the various pieces of apparatus.

## VI.—INCANDESCENT MANTLES

### (a) Thorium Nitrate.

Thorium nitrate, employed for the manufacture of incandescent mantles, has the composition,  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ , and, therefore, contains theoretically 47.85 per cent. of  $\text{ThO}_2$ . Pfeiffer finds that the commercial product almost invariably contains at least this percentage of oxide, and this may therefore be taken as a minimum value which ought to be reached in all deliveries. For the manufacture of mantles, sulphuric acid should be absent as far as possible, as only the nitrate yields a suitable oxide on ignition. Iron should be only present in traces, and chlorine should be absent, as, though in itself not specially objectionable, its presence is an indication of contamination with alkalis, which are most deleterious. Alumina, yttria, and ceria should also be absent, the presence of the latter being objectionable because it renders the

addition of the proper quantity of cerium nitrate for the manufacture of the mantles more difficult.

The analysis of the thorium nitrate is carried out by Pfeiffer as follows:—Seventy grams of the salt are dissolved in water and made up to 200 c.c., after filtration; each 10 c.c., therefore, contains 3.5 g. of thorium nitrate.

*Thoria.* Ten c.c. of the solution are diluted to 100 c.c., and 10 c.c. of the latter (=0.35 g.) evaporated in a platinum crucible, ignited at first gently and then strongly, and the residual  $\text{ThO}_2$  weighed.

*Sulphuric acid.* Twenty c.c. of the solution are diluted, precipitated with a slight excess of oxalic acid to remove thorium, and diluted to 300 c.c. The precipitate is filtered off without washing, and 150 c.c. of the filtrate (=3.5 g. nitrate) precipitated with barium chloride. If the thorium is not first removed, too high results are obtained.

*Chlorine* is determined by titration with  $N/10$  silver nitrate.

*Alumina.* Ten per cent. potassium hydroxide is added in excess to a portion of the solution, the precipitated hydroxide filtered off, and ammonium chloride added to the filtrate; if alumina is present, the liquid becomes opalescent.

*Iron* is most readily determined colorimetrically by means of potassium thiocyanate.

*Ceria.* A portion of the solution is diluted in a colorimeter tube and 1 c.c. of concentrated hydrogen peroxide solution (Merck's Perhydrol) added. On addition of ammonia, the thorium hydroxide precipitated is coloured orange if traces of ceria are present. In very dilute solution the cerium may be determined colorimetrically in this manner, citric acid being added to prevent the precipitation of the hydroxides, in which case a clear yellow solution is produced, the depth of colour being proportional to the amount of ceria present.<sup>1</sup>

*Didymia and Lanthana.* These bases may be tested for by adding 20 c.c. of 10 per cent. sodium carbonate solution to 10 c.c. of the thorium nitrate solution. The carbonates first precipitated should dissolve after a time, as the carbonates of yttrium and zirconium are sparingly soluble in excess of sodium carbonate, and that of thorium readily soluble. Any residue indicates the presence of didymia or lanthana, the carbonates of which are insoluble in sodium carbonate solution. As, however, cerium carbonate is also only slightly soluble, its absence must first be proved.

*Yttria and Zirconia.* A mantle made from the solution and placed on a Bunsen burner without a chimney should only give a sky-blue colour with but little luminosity.<sup>2</sup> A bright white light indicates the

<sup>1</sup> Cf. *Z. angew. Chem.*, 1902, 16, 300.

<sup>2</sup> Böhm (*Fabrikation der Glühkörper*, 1910, p. 28) states that a mantle of pure thoria has a characteristic reddish colour, but Pfeiffer does not agree with this statement.

presence of ceria, and a reddish or yellowish colour the presence of other earths. If other earths have been found to be absent, this is probably due to the presence of yttria and zirconia.

### (b) Mantles ready for use.

The quality of a mantle depends not only on the amount and relative proportions of thorium and ceria present, but also on the material and method of weaving of the fabric used in its manufacture. The chemical examination of the mantle has been of little value in most cases, as its quality is so greatly affected by the presence of traces of impurities which cannot be readily estimated. In some cases it is important to know the total amount of earths present, which in an unburnt mantle may be determined by extracting with hot water, filtering, and precipitating the filtrate with oxalic acid and a drop of nitric acid; the precipitate is ignited, and the oxides weighed.

Mantles which have been burnt off are heated with three times their weight of concentrated sulphuric acid on a sand-bath and poured into 20 c.c. of water. In twenty-four hours the sulphates dissolve completely, and the solution, after neutralising the excess of acid with ammonia, is precipitated with oxalic acid as described above.

The stability in shape of a mantle depends chiefly upon (a) the fabric employed and the method of weaving; (b) the alkali content; (c) the total quantity of earths, the stability increasing with the amount; (d) the manner in which the organic material is burned off. Alterations in the shape of the mantle result in a diminution of the illuminating power, as the mantle then no longer remains throughout in the hottest portion of the flame, and diminution of the light also follows from the gradual disappearance of the finer threads of oxides from the mantle.

For testing purposes, a number of mantles are picked out from a delivery and their illuminating power tested frequently over a lengthy period, and the manner in which this alters ascertained. So far as stability of shape is concerned, this is generally sufficiently evident after a burning period of four or five hours.

The stability of the mantles towards mechanical shocks is also greatly dependent on the nature and method of weaving of the fabric and on the total weight of oxides in the mantle. An apparatus for subjecting mantles to a series of shocks to test their stability has been devised by Woodall and Moon,<sup>1</sup> and a certain number of

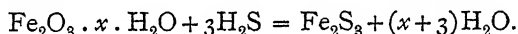
<sup>1</sup> Cf. J. H. Coste and W. E. F. Powney, *J. Soc. Chem. Ind.*, 1911, 30, 65. The apparatus is made by Messrs T. Glover & Co., Ltd., Edmonton.

mantles from a delivery are tested to destruction on this machine, which records the number of shocks necessary.

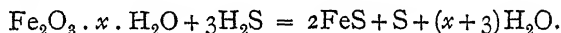
## VII.—PURIFICATION

Coal gas, after the removal of the ammonia, still contains a considerable amount of sulphuretted hydrogen, varying usually from 0.8 to 1.8 per cent., which must be removed from the gas completely before distribution, penalties being attached by statute to the presence of appreciable quantities of this impurity in the gas. In carburetted water gas the amount of sulphuretted hydrogen is lower, varying from 0.2 to 0.6 per cent. Carbon dioxide is also present in the scrubbed coal gas to the extent of 1 to 3 per cent., and in carburetted water gas of 3 to 6 per cent., but as this impurity is only a diluent and not otherwise deleterious, its removal is in most cases no longer carried out.

The purification from sulphuretted hydrogen is at present in most cases effected by passing the gas through moist, hydrated ferric oxide in dry purifiers. The sulphuretted hydrogen reacts in presence of alkali, forming ferric sulphide in accordance with the equation:—



If the gas is neutral or slightly acid, a mixture of ferrous sulphide and sulphur is formed:—



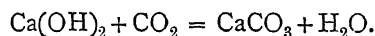
As the crude coal gas is always slightly alkaline from the presence of small amounts of ammonia, the first reaction usually occurs in the purifiers.

When the mass ceases to be active, it is removed from the purifier and exposed to moist air, the oxygen of which reconverts the ferric sulphide into oxide, with liberation of free sulphur. The revived mass is then recharged into the purifiers and again fouled, and the revivification and fouling continued alternately until the mass contains from 50 to 60 per cent. of sulphur, when it is sold for its sulphur content. The revivification of the ferric sulphide into oxide also goes on continuously in the purifier, owing to the presence of free oxygen in the gas, the most suitable proportion of oxygen being slightly above one-half the volume of the average percentage of the sulphuretted hydrogen present; when the oxygen accidentally drawn in does not reach this amount, more air is usually added. A rather higher percentage of oxygen is beneficial in increasing the amount of revivification *in situ*,

but the added nitrogen and excess of oxygen are objectionable on account of the increasing dilution of the gas produced. If the percentage of oxygen is very high, the oxidation of the mass may proceed so rapidly that the contained sulphur is partially fused; this leads to the formation of hard masses of the spent oxide, which can only be broken up and fully revived with difficulty; in some cases even combustion of the sulphur takes place, resulting in the fouling of the gas with sulphur dioxide.

Simultaneously with the absorption of the sulphuretted hydrogen, the hydrocyanic acid of the crude gas is partially absorbed by the ferric compounds present, with the formation of crude Prussian blue, which accumulates sufficiently in the spent material, in many cases, to make the product saleable for this constituent as well as for the sulphur.

The removal of carbon dioxide, when carried out, is effected by dry purification with slaked lime with which it combines, yielding calcium carbonate :—



The spent material in this case consists chiefly of calcium carbonate, which has frequently no commercial value, and costs considerable sums for its removal.

When the carbon bisulphide present in the gas has also to be partially removed, the impurities, carbon dioxide, sulphuretted hydrogen, and carbon bisulphide are all removed by means of slaked lime; the carbon dioxide is converted into calcium carbonate, and the sulphuretted hydrogen into calcium sulphhydrate,  $\text{Ca(SH)}_2$ , which, in presence of limited quantities of oxygen, effects a partial removal of the carbon bisulphide. The spent material obtained in this case consists of a mixture of calcium carbonate, sulphides, sulphate, thiosulphate, salts of other oxy-acids of sulphur, thiocyanate, and free sulphur, the sulphide present giving it a very objectionable odour, which gives rise to serious complaints as to nuisance, and renders the spent material very difficult to get rid of when produced in quantity. Largely on this account, the statutory compulsion to reduce the amount of carbon bisulphide has recently been repealed, and the removal is now much less frequently carried out than formerly. On the Continent, the removal of the bisulphide has seldom been carried out at any time.

## A. FRESH MATERIALS

### I. Oxide of Iron.

Natural bog-iron ore is most largely used in this country, but other forms of natural ore, and also artificial oxides are used to a considerable

extent, the latter being generally by-products from some other industry, such as the hydrated oxide of iron obtained in the preparation of pure alumina from bauxite.

All of these products, and especially the bog-iron ores, contain, in addition to the water in chemical combination with the ferric oxide as hydroxide, a considerable amount of free moisture, but it is impossible to ascertain exactly the proportion of water present in each condition, as the ferric hydroxide is usually present in the colloidal state, and the proportion of water to ferric oxide is not molecular, but varies according to the conditions. It is, however, customary to regard all moisture which is evolved on heating at  $100^{\circ}$  as "free" moisture, and that given off on further heating as "combined" moisture. The composition of the ferric hydroxide, dried at  $100^{\circ}$ , corresponds approximately to the formula,  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , but it is doubtful whether this is a definite chemical compound. Bog-iron ores always contain large amounts of organic matter. The other oxides are usually mixed with sawdust or similar material to render them more porous.

The determination of the percentage of ferric oxide in a sample does not give any conclusive indication of its value for purification purposes, as this depends largely upon the physical condition, as well as on the amount of the iron oxide present, and samples containing a high percentage of oxide are often much less suitable for purification than those containing a lower proportion. More valuable information in this respect is obtained by determining the amount of sulphuretted hydrogen which a sample will take up when completely saturated with the gas.

For the control of the quality of such oxide supplied under contract, it is, however, frequently specified in the contract notes, that not only shall the moisture evolved at  $100^{\circ}$  not exceed a specified amount, but also that the material thus dried shall contain a specified minimum of ferric oxide. The bog-iron ores contain large quantities of free moisture up to as much as 60 per cent., and a limit varying from 40 to 50 per cent. is frequently specified, with the further condition that the amount of ferric hydroxide in the dried material, calculated as  $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , shall also fall below an amount varying from 60 to 70 per cent.

*Sampling.* As the materials, and especially the natural bog-iron ores, often vary very greatly in composition in different portions of the same consignment, especial care must be taken in sampling the bulk, and in sampling down from the first bulk sample to a quantity of 400 to 500 g. (*cf.* Vol. I., pp. 9 *et seq.*).

*Free Moisture.* From 200 to 250 g. are crushed in a mortar and the often pasty mass forced by the pestle through a stout sieve of about 10 meshes to the inch, and the product carefully mixed. This operation



should be carried out as quickly as possible in a cool, moist atmosphere to avoid loss of moisture from evaporation. From 10 to 20 g. of the prepared sample are then dried in a water oven at 100° till no further loss of weight occurs (two to two and a half hours), the loss of weight being calculated as free moisture.

*Analysis of the Dried Material.* From 100 to 200 g. of the material which has been passed through the 10-mesh sieve are dried in a basin on the water-bath until sufficiently dry to powder readily; it is then ground to pass through a sieve of 60 meshes to the inch, the sifted product well mixed, and about 10 g. dried in the water-oven till no further loss of weight takes place.

*Combined Water and Organic Matter.* About 0.5 g. of the dried powder is gently ignited in a platinum crucible till all carbonaceous matter has burned off; the loss of weight gives the total amount of combined water and organic matter.

*Ferric Oxide and Silica.* The ignited residue is ground to a very fine powder with a little water in an agate mortar, washed into a beaker with a small quantity of water, and boiled with 20 c.c. of pure concentrated hydrochloric acid until the residual silica is quite white. If the latter is to be determined, the solution is evaporated to dryness on the water-bath, the residue moistened with hydrochloric acid, the silica filtered off, washed, and weighed in the usual manner. In the filtrate, or if the silica determination is not required in the original hydrochloric acid solution, the amount of iron is determined by reduction by any of the usual methods and titration with  $N/10$  bichromate solution.

*Absorptive power for Sulphuretted Hydrogen.* A portion of the sample which has passed through the 10-mesh sieve is placed in a weighed U-tube, which is again weighed to ascertain the weight of oxide taken. This is connected with a second U-tube containing calcium chloride, and the two tubes weighed together. A slow current of sulphuretted hydrogen from a Kipp or similar apparatus, previously dried with calcium chloride, is then passed through the U-tubes till these undergo no further increase of weight. Dry air is then drawn through the tubes to replace the sulphuretted hydrogen, and the tubes again weighed; the increase of weight gives the amount of sulphuretted hydrogen taken up by the oxide. The percentage absorbed is preferably calculated on the dried oxide; it gives an indication of the comparative value of the sample for purification purposes, a convenient method being to compare the figure thus obtained, in all cases, with that found by the same treatment with a known and tried sample of good material.

The use of crude gas in place of pure sulphuretted hydrogen is not advisable, as the former always contains oxygen, which effects a partial revivification of the ferric sulphide, and as the percentage of oxygen

varies considerably from time to time, it is impossible to test different samples under uniform conditions.

If the material is very wet, it is advisable to allow it to dry somewhat in a desiccator over sulphuric acid before passing sulphuretted hydrogen, due allowance for the water lost being made in the subsequent calculations.

## 2. Lime.

The lime employed for the removal of carbon dioxide should be a well-burnt, readily-slaking, non-hydraulic lime, free from stone and other impurities and containing about 90 per cent. of calcium oxide and not more than 1 to 2 per cent. of carbon dioxide. The methods of analysis are fully described in Vol. I., pp. 658 *et seq.*

For gas purification purposes, where it is desired to determine the amount of lime present as oxide, excluding that present as carbonate, a convenient method is to warm the finely powdered sample with a solution of cane sugar, which dissolves the oxide, forming a solution of calcium saccharate, but leaves the carbonate undissolved. The filtered solution is then titrated with normal hydrochloric acid, using methyl orange or phenolphthalein as indicator.

## B. USED MATERIALS

### 1. Spent Oxide.

The analysis of the spent and partly spent oxide is frequently necessary: on the one hand, for control of the purifying process in order to ascertain the extent to which the material has taken up sulphuretted hydrogen and whether it is completely spent and ready for sale, and on the other hand, for the valuation of the product previous to sale.

The only determinations usually necessary are those of free moisture, sulphur, and the percentage of Prussian blue; only the first two are ordinarily required in the control of the purification processes. Occasionally, for special purposes, the amount of ammonium thiocyanate is also determined.

*Sampling.* As with the fresh oxide, the composition of the spent material is apt to vary considerably throughout the mass, and to obtain a representative sample, the rules of sampling given in Vol. I., pp. 9 *et seq.*, must be carefully adhered to.

*Free Moisture.* About 300 to 400 g. of the bulk sample are ground to pass through a sieve of 10 meshes to the inch, well mixed, and sampled down to 50 to 100 g. About 10 g. of the product is heated in a water-oven at 100° for about one and a half hours, and the loss of weight taken as "free" moisture. In addition to the water, some of the cyanogen products present may undergo decomposition with loss of

hydrocyanic acid at this temperature, so that the loss may not be entirely due to water. Spent oxide, thus dried, must not be employed for the cyanide estimation, undried material being always taken for this purpose, or only such as has been dried at the ordinary temperature over sulphuric acid in a desiccator. Further, the drying must not be continued for much longer than one and a half hours, as sulphur is slowly but appreciably volatile at 100°.

*Sulphur.* For purification control purposes, and also as between buyer and seller, the estimation of free sulphur is almost always made by extracting the latter with carbon bisulphide, as although the method is not free from objection, it is readily carried out, and gives results of sufficient accuracy for ordinary purposes, especially in view of the fact that the material is not a commodity which commands a high price.

For the extraction of the sulphur, about 10 g. of the spent oxide are dried, placed in a Soxhlet filter sheath, and extracted in a Soxhlet apparatus with boiling carbon bisulphide into a weighed flask. After extraction, the carbon bisulphide is distilled off as completely as possible on the water-bath, air drawn through the flask whilst still in the water-bath for about ten minutes, the residual sulphur heated carefully on a sand-bath till it is just melted, and the flask allowed to cool, and weighed; the increase of weight of the flask gives the weight of sulphur in the spent oxide taken. From this, and from the known weight of spent oxide taken and its moisture content, the percentage of sulphur both in the undried and dried material can be calculated; the former is termed the percentage on the *wet basis*, and the latter that on the *dry basis*.

The carbon bisulphide employed for the extraction must be recently distilled, as free sulphur gradually forms in the liquid on exposure to light.

The chief source of error in the method arises from the fact that the spent oxide almost invariably contains tarry matter, a considerable proportion of which is extracted, together with the sulphur, by the bisulphide. Where the quantity is large, which is generally noticeable from the dark colour of the extract, and the difficulty with which the extracted sulphur solidifies after fusion, a portion of the latter is oxidised by heating with fuming nitric acid on the water-bath for some hours, and the sulphur, thus oxidised to sulphuric acid, estimated by precipitation as barium sulphate. Pfeiffer effects the purification of the sulphur from tarry matter by adding about 1 g. of blood charcoal to the carbon bisulphide solution before evaporation, allowing to stand overnight, and then evaporating after filtering off the charcoal.

Some spent oxide buyers specify that the extraction must be carried out with cold carbon bisulphide, holding that the hot liquid effects a more complete removal of the tarry matters than is the case with the

cold solvent. For this purpose, about 2 g. of the dried sample are placed in an ordinary filter paper and funnel, and extracted with cold bisulphide, which is run on to the filter from a separating funnel, the stem of which passes through a hole in a clock-glass with which the funnel is covered; 500 c.c. of carbon bisulphide effect a practically complete extraction.

## 2. Cyanogen.

As already mentioned, the ferric oxide always absorbs some of the hydrocyanic acid of the crude gas, and the spent oxide contains various cyanogen compounds, the most important of which are the insoluble double ferrocyanides of iron and ammonium, generally classed together as Prussian blue. In addition, derivatives of carbonylferrocyanic acid,  $\text{H}_3\text{FeCO}(\text{CN})_5$ , are usually present, as well as thiocyanate; the quantity of the thiocyanate increases and that of ferrocyanides decreases as the quantity of ammonia in the gas entering the purifier increases. The only products of value from the commercial point of view are the ferrocyanides, though in many cases the carbonylferrocyanides are included in the analysis and returned as ferrocyanides. The thiocyanates can be recovered by extraction with water, but the product is so impure that its working up is now rarely carried out.

*Ferrocyanide.* For the determination of the ferrocyanide content, 40 g. of the undried, average sample of the material is placed in a capacious mortar with about 100 c.c. of water and 40 g. of sodium hydroxide, well triturated with the pestle, and the whole allowed to stand for some hours with occasional trituration; the insoluble ferrocyanides and carbonylferrocyanides are thus converted into the soluble sodium salts. Heating the mixture must be avoided, as considerable quantities of sodium sulphide are formed, and the latter, in presence of ammonia, effects a partial conversion of the ferrocyanides into thiocyanate. It is sometimes preferred to remove the sulphur by extraction with carbon bisulphide previous to treatment with sodium hydroxide, in which case there is less danger in heating the solution. Some samples of spent oxide contain very small amounts of insoluble ferrocyanide, probably in the form of ferrous ferrocyanides, which are not rendered soluble even on heating, but as these are also not recovered in the large scale working up of the products, the error thus caused is not of importance.

The contents of the mortar are then diluted, and either filtered and made up to 1000 c.c., or made up directly to 1000 c.c. plus a volume of water approximately equal to that of the solid matter present, and an aliquot portion of the clear solution taken for analysis.

If the carbonylferrocyanides present are to be included in the analytical result as ferrocyanide, 25 c.c. of the clear solution (= 1 g. of

spent oxide) are made slightly acid with sulphuric acid, an excess of iron alum solution added, and the mixture heated to  $60^{\circ}$ , but not higher, as otherwise loss of hydrocyanic acid may occur. The precipitated Prussian blue is filtered off, preferably by using a folded filter paper. Sometimes a small quantity of the precipitate passes at first through the filter; this must be refiltered and the refiltration continued until a small portion of the filtrate shows no blue coloration after destroying the colour of the ferric thiocyanate by addition of mercuric chloride. The precipitate is washed once or twice with water containing ammonium sulphate, the filter and precipitate transferred to a beaker, and decomposed by addition of a slight excess of potassium hydroxide solution. On filtering from the precipitated ferric hydroxide and washing, a fairly pure solution of ferrocyanide is obtained suitable for analysis.

If carbonylferrocyanides are to be removed, 25 c.c. of the clear, original solution are mixed with 150 c.c. of methylated spirit, which precipitates the whole of the ferrocyanide together with any sulphate, carbonate, or chloride present, whilst the whole of the sulphide, thiocyanate, carbonylferrocyanide and excess of alkali remain in solution. Precipitation is complete in an hour, but it is preferable, if possible, to allow the mixture to stand overnight, as it then filters much more readily. The precipitated ferrocyanide is filtered off, washed with alcohol, dried at  $100^{\circ}$ , and redissolved in water.

For the estimation of ferrocyanide in the solutions thus purified, three types of method are employed:—(1) Direct estimation of the ferrocyanide by precipitation with a solution of a suitable metallic salt; (2) Estimation of the amount of iron in the solution, and calculating from it the amount of ferrocyanide; (3) Estimation of the hydrocyanic present.

1. *Direct Estimation of the Ferrocyanide by precipitation.* This method, originally proposed by Bohlig,<sup>1</sup> and more completely worked out by Knublauch,<sup>2</sup> consists in titrating the solution, acidified with sulphuric acid, with a standard solution of copper sulphate, which precipitates the ferrocyanide as copper ferrocyanide, the addition of the copper solution being continued until a drop of the clear solution no longer gives a blue coloration with ferric chloride. In place of copper sulphate, a solution of zinc sulphate may be used, the method being the converse of that for the estimation of zinc by means of potassium ferrocyanide. Bohlig originally employed a solution of 10 g. of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  per litre, but one of 30 g. per litre is more generally convenient. For the zinc sulphate solution, Skirrow<sup>3</sup> finds that a strength of 46.5 g. of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  per litre is most suitable. The

<sup>1</sup> *Polytech. Notizblatt.*, 1861, 16, 81.

<sup>2</sup> *J. Gasbeleucht.*, 1889, 33, 450.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1910, 29, 319.

solution, in either case, is standardised with pure potassium ferrocyanide.

To carry out the titration, the solution of ferrocyanide, previously freed from sulphide, if present, by shaking with lead carbonate and filtration, is placed in a basin, acidified with sulphuric acid, and the copper or zinc solution added from a burette, with constant stirring, until the clear solution no longer gives a blue coloration with an acidified solution of ferric chloride or sulphate. The end-point of the reaction may be ascertained either by filtering small portions of the solution through Swedish filter paper, and adding the ferric solution to the filtrate (mercuric chloride being also added to destroy the colour of ferric thiocyanate if present), or, a drop of the clear liquid may be placed on thick filter paper free from iron (*e.g.*, Schleicher and Schüll's drop reaction paper, No. 601), followed by a drop of the ferric solution placed so that it only comes in contact with the clear portion of the spot and not with the precipitate. Both plans give good results provided that the same time (one half-minute, one minute, or two minutes) is always allowed for the development of the blue coloration, both in standardising and in titrating, but the drop reaction paper is the more rapid and convenient. A slightly larger quantity of copper and zinc solution is always used both in standardising and in the analysis when the filtration method is employed.

This method gives good results, if certain conditions are rigidly adhered to, but not otherwise. The precipitate formed consists, not of pure copper or zinc ferrocyanide, but of a colloidal double ferrocyanide of these metals with those of the other soluble salts present in the solution, and the composition of this precipitate and consequently the amount of copper or zinc solution used, varies considerably both with the nature and amount of such other salts present.<sup>1</sup> For correct results it is essential that in the ferrocyanide solution tested, this shall be present as the same salt as that used for standardising the solution, and that approximately the same weight of other potassium or sodium salts should be present. With the copper solution, the error caused by non-adherence to this condition may amount to more than 10 per cent., but with that of zinc this error is much less.

As potassium ferrocyanide is the salt most readily obtained in a state of purity it is usually employed for standardising, and consequently the ferrocyanide must then always be converted into the potassium salt before analysis. With ferrocyanides of the alkaline earths this may be done by precipitation with potassium carbonate solution, but with the sodium and ammonium salts it is necessary to precipitate the ferrocyanide as Prussian blue and decompose the latter with potassium hydroxide. As, however, an excess of alkali must

\* <sup>1</sup> Colman, *Analyst*, 1908, 33, 261.

always be used for the latter purpose, and this is converted into sulphate on acidifying with sulphuric acid, a larger amount of potassium sulphate is present in the solution titrated than when standardising with pure potassium ferrocyanide, which tends to make the result obtained rather low.

This tedious precipitation as Prussian blue and decomposition by potassium hydroxide may be obviated, and substantially correct results obtained with any ferrocyanide salt, if the standardisation and analysis are carried out in the presence of a considerable excess of potassium sulphate, as the effect of this salt is much greater than that of the other soluble sulphates.<sup>1</sup> According to this method, the copper or zinc sulphate solution is standardised by a weight of potassium ferrocyanide approximately equal to that in the solution to be analysed, which is mixed before titration with 50 c.c. of a cold, saturated solution of potassium sulphate (containing about 5 g.  $K_2SO_4$ ). The solution to be analysed, which may then contain the ferrocyanide as any soluble salt, is similarly mixed with 50 c.c. of the saturated potassium sulphate solution before titration. The titration should be carried out rapidly, as on standing the precipitated ferrocyanide slowly undergoes change, some ferrocyanide passing into solution.<sup>2</sup>

Where the ferrocyanide solution is obtained by decomposing Prussian blue with potassium hydroxide, the solution frequently contains iron other than that present as ferrocyanide, which on addition of sulphuric acid forms sulphate and precipitates a small quantity of Prussian blue, thus tending to make the results low. In such cases Skirrow recommends the concentration of the solution to a small bulk, and filtering before acidifying; the iron not present as ferrocyanide is thus largely removed.

2. *Estimation of the Iron in the Ferrocyanide Solution.* This method, due to Rose<sup>3</sup> and Leybold and Moldenhauer,<sup>4</sup> consists in evaporating the dry ferrocyanide with concentrated sulphuric acid, whereby the iron is converted into ferric sulphate, in which form the iron is readily determined, either gravimetrically or volumetrically, by any of the commonly employed methods. A more convenient method of converting the iron into ferric sulphate, especially where this is in solution and would otherwise have to be evaporated, is that of Dittrich and Hassel,<sup>5</sup> according to which the solution is slightly acidified with sulphuric acid, 2 to 3 g. of ammonium persulphate added, and the liquid boiled for twenty to thirty minutes. If any blue colour then persists, it may be removed by addition of hydrochloric acid and a little more persulphate. The iron is precipitated by ammonia as hydroxide and estimated either gravimetrically or volumetrically.

<sup>1</sup> Colman, *Analyst*, 1908, 33, 265. <sup>2</sup> Cf. Skirrow, *loc. cit.* <sup>3</sup> *Z. anal. Chem.*, 1862, 1, 194.

<sup>4</sup> *J. Gasbeleucht.*, 1899, 33, 153.

<sup>5</sup> *Ber.*, 1903, 36, 1929.

With fairly pure salts, containing only small quantities of other salts such as sulphates, this method gives excellent results, but it is unsuitable for crude gasworks products, as these and the solutions obtained from them mostly contain iron in forms other than ferrocyanide, and the results may, therefore, come out decidedly high.

3. *Estimation of the Hydrocyanic Acid.* The method adopted for this purpose was originally proposed by Rose and Finkener,<sup>1</sup> and has been further developed by Feld.<sup>2</sup> It depends upon the fact that mercuric oxide converts a boiling solution of a soluble ferrocyanide into mercuric cyanide, from which the hydrocyanic acid may then be recovered by distillation with sulphuric acid in presence of chlorides.

To carry out the determination, a solution containing about 0.3 to 0.5 g. of potassium ferrocyanide or its equivalent, freed from sulphide if necessary with lead carbonate, is diluted to about 150 c.c., 10 c.c. of normal sodium hydroxide solution added, and the mixture heated to boiling. Fifteen c.c. of 3*N* magnesium chloride solution are then added in a thin stream, and the boiling continued for five minutes. (If any hydrocyanic acid is present as cyanide, it is evolved at this stage, and may be condensed, collected, and determined by titration with *N*/10 silver nitrate, the boiling in that case being continued for ten minutes.) One hundred c.c. of boiling *N*/10 mercuric chloride solution are then added, and the boiling continued for a further ten minutes, after which the flask is connected to a condenser, 30 c.c. of 4*N* sulphuric acid run in by means of a stoppered funnel, and distillation continued for twenty to thirty minutes, the end of the condenser dipping under the surface of 25 c.c. of sodium hydroxide solution placed in the receiver. In this manner the hydrocyanic acid present as ferrocyanide is obtained in the receiver as a solution of sodium cyanide, the amount of which is determined by dilution to 300 to 400 c.c., adding a little potassium iodide, and titrating with *N*/10 silver nitrate until a permanent yellow precipitate of silver iodide is formed. Each cubic centimetre of silver nitrate solution equals 0.005403 g. of hydrocyanic acid, 0.01408 g.  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ , 0.01614 g. of  $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ , or 0.00955 g. of  $\text{Fe}_7(\text{CN})_{18}$ .

The Feld method of estimation has been found by many analysts to give accurate results, whereas Skirrow<sup>3</sup> states that loss of hydrocyanic acid takes place during the boiling with magnesium chloride and also during the later stages, either in the formation of mercuric cyanide, or in the distillation with sulphuric acid. Colman<sup>4</sup> finds that such loss is very slight under ordinary circumstances, and his results show that when the above conditions as to the length of time for which

<sup>1</sup> *Z. anal. Chem.*, 1862, 1, 299.

<sup>2</sup> *J. Gasbeleucht.*, 1903, 47, 565.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1910, 29, 319.

*Analyst*, 1910, 35, 295.



the solution is boiled are adhered to, the results are substantially accurate.

If the carbonylferrocyanides have not been previously removed by treatment with alcohol in the manner described above, their presence affects the estimation of ferrocyanides by all these methods, as they are precipitated by copper and zinc salts, and the contained iron and cyanogen are determined together with that present as ferrocyanide in the last two methods given. Usually, the amount of carbonylferrocyanide is small, amounting on the average to about 3 per cent. of the ferrocyanide, but in exceptional cases it may amount to 20 per cent.

### 3. Ammonia.

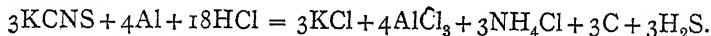
The ammonium compounds soluble in water contained in the spent oxide may be estimated by triturating 50 g. of the material with 100 c.c. of water in a mortar, and allowing to stand, with occasional trituration, for several hours; the solution is then made up to 500 c.c. plus about 15 c.c. allowance for the insoluble matter present. A little magnesium chloride solution added before making up to the standard volume, facilitates the subsequent filtration. An aliquot portion of the solution, filtered through a dry filter, is then distilled with sodium hydroxide into normal sulphuric acid as described under ammoniacal liquor (p. 733).

The total ammonia present may be determined in a similar manner by distillation of 10 g. of the spent oxide with sodium hydroxide, the difference between the two determinations giving the amount of ammonia present in the form of insoluble ammonium iron ferrocyanides.

### 4. Thiocyanate.

The aqueous solution obtained as in the estimation of the soluble ammonium compounds may be employed for the estimation of the thiocyanate. Fifty c.c. (= 5 g. spent oxide) are precipitated as cuprous thiocyanate and titrated with silver nitrate, according to the method already described (677).

Another method, depending on the fact that the sulphur in thiocyanate is evolved as sulphuretted hydrogen when the solution is boiled with aluminium and hydrochloric acid, has been described by Feld.<sup>1</sup> The reaction is:—



The sulphuretted hydrogen given off is titrated with iodine and starch. Thiosulphates must first be destroyed by boiling with a solution of magnesium and mercuric chlorides.

<sup>1</sup> *J. Gasbeleucht.*, 1903, 46, 561.

### 5. Crude Prussian Blue and other Cyanogen Products obtained in Gasworks.

In some gasworks special processes are adopted for the recovery of the hydrocyanic acid before the purifiers, either as ferrocyanide or thiocyanate (p. 675).

The analysis of the various ferrocyanide products is carried out by the methods described for the estimation of ferrocyanides in spent oxide.

The analysis of the thiocyanate solution obtained in the British Cyanide Co.'s process, is carried out by precipitation as cuprous thiocyanate, conversion of the latter into sodium thiocyanate, and titration with  $N/10$  silver nitrate by Volhard's method, as described on p. 677.

## VIII.—AMMONIACAL LIQUOR

The aqueous condensates from the hydraulic main, foul main, and condensers, termed together "virgin liquor," and the ammoniacal liquor obtained by treatment of the gas with fresh water in the washers and scrubbers, are usually collected together in a common well or wells. The combined liquor contains practically the whole of the ammonia present in the crude gas, together with a considerable amount of the sulphuretted hydrogen and carbon dioxide present in the latter.

The liquor rarely, if ever, contains ammonia in the free state (*i.e.*, as hydroxide); it is usually entirely present as salts, of which the different sulphides and carbonates of ammonium constitute much the largest amount, whilst the chloride, thiocyanate, sulphate, thiosulphate, cyanide, and ferrocyanide are usually present in smaller quantity. The products primarily formed are the sulphides, carbonates, cyanide, and chloride, these being obtained from the sulphuretted hydrogen, carbonic acid, hydrocyanic acid, and hydrochloric acid respectively, contained in the crude gas; the other salts are formed from these by secondary reactions. The oxidation of the sulphides gives rise in the first instance to thiosulphate and polysulphide, but the latter immediately combines with ammonium cyanide, forming the thiocyanate. The latter compound is also formed to a smaller extent by the combination of the ammonium sulphides with the carbon bisulphide of the crude gas, to form ammonium thiocarbonate, which then undergoes conversion into thiocyanate. Ammonium cyanide also probably acts on the thiosulphates to some extent forming ammonium thiocyanate and sulphite, and also attacks the iron of the apparatus slightly, forming ammonium ferrocyanide. The sulphites, and probably the thiosulphates, undergo slow oxidation to sulphate.

Polysulphide is rarely found in ammoniacal liquor, owing to its

reaction with the ammonium cyanide present, and the latter is also usually, for the most part, converted into thiocyanate in liquor which has been stored for some time. The presence of free cyanide in liquor has often been denied, but Linder has shown that it is frequently present even in stored gasworks liquor. Coke oven liquors, in which case but little storage is practised, and, therefore, little time allowed for the production of polysulphide by oxidation of the sulphide, often contain large amounts of cyanide, and, on working up the liquor into ammonium sulphate, the waste gases may retain very considerable amounts of hydrocyanic acid, and become dangerous on account of the poisonous nature of this gas.<sup>1</sup>

In addition, the liquor always contains a considerable quantity of organic matter, of which the phenols form the largest proportion, and small amounts of nitrogenous bases, such as pyridine, and probably also amino-derivatives.

The ammonia present as sulphide, carbonate, and cyanide is distinguished as "volatile" ammonia, inasmuch as the ammonia present in this form is completely volatilised on boiling the liquid; the remainder is termed "fixed" ammonia, as it can only be driven off by addition of a sufficient amount of a stronger alkali to combine with the whole of the remaining acid radicals present. In the combined gasworks liquor, some 75 to 80 per cent. of the ammonia is usually present in the "volatile" form; in the virgin liquor the proportion of "fixed" ammonia often amounts to 50 per cent. of the whole.

*Strength of Ammoniacal Liquor.* For the most part, the only determination made of the liquor is the total quantity of ammonia present, and in this country the strength is usually expressed by stating the number of ounces (by weight) of sulphuric acid required to neutralise the ammonia present in 1 gallon of the liquor, this figure being known as the "oz. strength." Thus, for example, if a gallon of liquor requires 9.3 oz. of sulphuric acid per gallon, this would be known as 9.3 oz. liquor. For statistical purposes, such as expressing the yield of ammonia per ton of coal carbonised, or for the sale of liquor in bulk, it is customary to convert all quantities of such liquor into the equivalent volume of "10 oz. liquor."

The following figures may be employed to obtain more generally familiar figures from those given in terms of oz. strength:—

$$\begin{aligned}\text{Oz. strength} &= 4.61 \times \text{grams } \text{NH}_3 \text{ per } 100 \text{ c.c.} \\ 1 \text{ gall. of } 10 \text{ oz. liquor} &= 1518 \text{ grains or } 0.2169 \text{ lb. } \text{NH}_3 \\ &= 0.8412 \text{ lb. } (\text{NH}_4)_2\text{SO}_4.\end{aligned}$$

*Specific Gravity of Ammoniacal Liquor.* As the ammonia is always present in the form of salts, the specific gravity of the liquor is

<sup>1</sup> Cf. *Report on Alkali, etc., Works*, 1906, p. 33.

always greater than water, and contrary to the case of solutions of pure ammonia, it increases with an increase in the contained ammonia. For the purpose of the control of the working of the washers and scrubbers, the strength of the liquor is always inferred from its density, as determined by Twaddell's hydrometer, it having been found that each degree Tw. corresponds approximately to 2 oz. strength of liquor, so that the oz. strength is found roughly by doubling the Twaddell hydrometer reading. Naturally, owing to the varying proportions of the ammonium salts present, this estimate is only of a very approximate nature, and although sufficiently accurate for works control purposes, is quite inadmissible if any degree of accuracy is required. Thus, a liquor showing 5° Tw. and taken as 10 oz. strength may vary actually between 8 oz. and 12 oz. in extreme cases, and in the case of virgin liquor especially, the strength inferred from the density is much too high.

#### A. ANALYSIS OF AMMONIACAL LIQUOR

**1. Total Ammonia.**—For the exact estimation of the ammonia, the usual method of distilling it off in presence of an excess of fixed alkali, and collecting the distillate in a known volume of standard acid, is almost invariably employed.

For this purpose, 10 c.c. to 25 c.c., according to the strength of the liquor, is placed in a flask, diluted to about 200 to 250 c.c., 20 c.c. of 5 per cent. sodium hydroxide solution added, and the liquid distilled for about twenty minutes, or until about 150 c.c. have passed over. The liquid must not be distilled to dryness, as otherwise some ammonia may be formed by the decomposition of thiocyanates, etc. The distilling flask is provided with a drop-catching bulb, as shown in Fig. 117, to prevent the mechanical carrying over of drops of the alkaline solution, and the steam, etc., may be passed through a condenser and the distillate collected in 25 c.c. of normal sulphuric acid. Or, the vapours may be passed, without condensation, direct into the normal acid, with equally correct results, provided precautions are taken to prevent the mechanical loss of the liquid by spurting. This may be done by fitting the receiver with a doubly-bored rubber stopper, the delivery tube from the distilling flask passing through one hole, and the other carrying a calcium chloride tube filled with broken glass, care being taken that the glass used has not an alkaline reaction. At the conclusion of the distillation, the contents of the receiver, cooled if necessary, are titrated with normal sodium hydroxide, using methyl orange as indicator. The difference between the volume of  $N/1$  alkali required and the volume of sulphuric acid taken represents the number of cubic centimetres of sulphuric acid neutralised by the ammonia in the quantity of liquor

taken, each cubic centimetre being equal to 0.01703 g. of  $\text{NH}_3$ . For example, 10 c.c. of liquor were taken, and distilled into 25 c.c. of  $N/1$

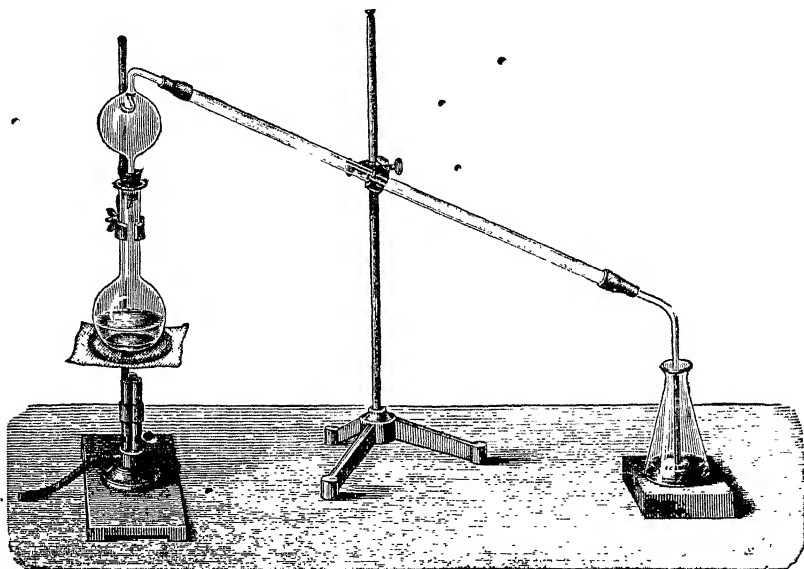


FIG. 117.

$\text{H}_2\text{SO}_4$ , and 12.2 c.c. of  $N/1$   $\text{NaOH}$  were required for the neutralisation of the distillate. Then:—

Grams ammonia per 100 c.c.

$$= \frac{(25 - 12.2) \times 0.01703 \times 100}{10} = 2.18 \times 4.61 = 10.05 \text{ oz.}$$

**2. Volatile Ammonia.**—For the separate determination of the volatile ammonia, the analysis is carried out in exactly the same manner as above, with the omission of the addition of sodium hydroxide to the liquor before distillation. On continuing the distillation for a longer period than there given (twenty minutes), traces of ammonia continue to come over for a long time: these are, however, probably not ammonia present as sulphide and carbonate, but result from the decomposition of the organic nitrogenous compounds present in the liquor.

Direct determination of the volatile ammonia, by titrating the liquor with sulphuric acid, using methyl orange as indicator, does not give satisfactory results, the end-point of the reaction being very uncertain.

**3. Fixed Ammonia.**—This may be determined by addition of sodium hydroxide to the residue in the distillation flask after the determination of the volatile ammonia, or by deducting the amount of volatile ammonia from the total ammonia.

## B. COMPLETE ANALYSIS

The analysis of the remaining constituents of the ammoniacal liquor is not required in the ordinary gasworks routine, but is of use for special purposes. The first full scheme of analysis was proposed by Dyson,<sup>1</sup> but the subject was much more completely worked out by Linder.<sup>2</sup> Mayer and Hempel<sup>3</sup> have also studied the subject, and come to conclusions which are substantially in agreement with those of Linder.

The estimation of total, volatile, and free ammonia is carried out as described above; the methods for the remaining constituents are as follows:—

**1. Carbonic Acid.**—Ten c.c. of liquor (or more if dilute) are diluted to 400 c.c. in a flask fitted with a Bunsen rubber valve, 10 c.c. of ammoniacal calcium chloride solution (1 c.c. = 0.044 g.  $\text{CO}_2$ ) added, and the whole heated on a water-bath for one and a half to two hours. The precipitated calcium carbonate is filtered off, washed, the precipitate washed back into the flask, dissolved in a known volume of  $N/2$  hydrochloric acid, and the excess of acid titrated back with  $N/2$  sodium carbonate, using methyl orange as indicator. The small amount of calcium carbonate remaining on the filter is best recovered by incineration, the ash being placed in the flask before adding the acid.

Grams  $\text{CO}_2$  per 100 c.c. =  $0.011 \times 10 \times \text{c.c. of } N/2 \text{ acid used}$ .

**2. Hydrochloric Acid.**—Ten c.c. of liquor are diluted to 150 c.c., boiled to remove volatile ammonia, and then boiled for a further fifteen minutes with addition of 25 c.c. of hydrogen peroxide (10 vols.). Five or six drops of 10 per cent. potassium chromate solution are then added, and the whole boiled for two minutes, after which a slight excess of sodium carbonate is added, and the boiling continued for one minute. The filtered and cooled solution is made up to 250 c.c., and an aliquot portion titrated with neutral  $N/10$  silver nitrate, after neutralisation with dilute nitric acid.

Grams HCl per 100 c.c. =  $0.00364 \times 10 \times \text{total c.c. } N/10 \text{ AgNO}_3$ .

A blank experiment should be made with 10 c.c. of  $N/10$  sodium chloride solution, and the same volumes of water, peroxide, chromate, and carbonate, to determine the correction for traces of chloride in the reagents used. If, however, Merck's perhydrol is used and pure sodium carbonate solution, this correction is, as a rule, unnecessary.

Sometimes the organic matter resists oxidation, in which case more

<sup>1</sup> *J. Soc. Chem. Ind.*, 1883, 2, 229.

<sup>2</sup> *Reports on Alkali, etc., Works*, 1902, p. 71; 1903, p. 31; 1904, p. 27; 1905, p. 26; 1906, p. 33; 1907, p. 53; 1908, p. 17; 1909, p. 15.

<sup>3</sup> *J. Gasbeleucht.*, 1908, 51, 381.

hydrogen peroxide must be added, and the boiling continued for a longer time.

**3. Sulphuric Acid.**—Two hundred and fifty c.c. of the liquor are concentrated to about 10 c.c., 2 c.c. of concentrated hydrochloric acid added, and the evaporation continued to decompose the thiosulphate, and render the organic matter less soluble. The residue is extracted with water, filtered, made up to 250 c.c., and 100 c.c. precipitated as barium sulphate in the usual manner.

$$\text{Grams H}_2\text{SO}_4 \text{ per 100 c.c.} = \text{BaSO}_4 \times 0.4202$$

$$,, \text{ S as H}_2\text{SO}_4 \text{ per 100 c.c.} = \text{BaSO}_4 \times 0.1374.$$

**4. Sulphuretted Hydrogen.**—According to Linder, 10 c.c. of the liquor (or more if dilute) is added to an excess of an ammoniacal zinc chloride solution, diluted to about 80 c.c. with warm water, the solution heated to about 40° to coagulate the zinc sulphide, which is then filtered, and washed with water at 40° to 50°. The zinc sulphide is washed from the filter into an excess of *N*/10 iodine solution mixed with hydrochloric acid, the last traces being dissolved from the filter by cold dilute acid. After vigorous shaking to effect complete solution of the zinc sulphide, the excess of iodine is determined by titration with *N*/10 sodium thiosulphate and starch.

$$\text{Grams H}_2\text{S per 100 c.c.} = 10 \times 0.0017 \times \text{c.c. } N/10 \text{ iodine used}$$

$$,, \text{ S as H}_2\text{S per 100 c.c.} = 10 \times 0.0016 \times \text{c.c. } N/10$$

Mayer and Hempel prefer to employ a cold solution of ammoniacal zinc acetate for precipitation of the zinc sulphide, and to wash with cold water containing ammonium salts, but otherwise they proceed in the same manner as Linder.

**5. Sulphite and Thiosulphate.**—Linder finds that no exact method of determination of these constituents in liquor is possible based on the use of iodine, save in exceptional cases. A united figure for these two constituents may be obtained by difference by subtracting the amount of sulphur present as sulphate, thiocyanate, and sulphide from the total sulphur content.

Mayer and Hempel have suggested the determination of the following data as an approximate method:—The total quantity of iodine taken up by the original liquor is first ascertained, the number of cubic centimetres required being noted by A. To get a definite end-point in the reaction, the acidified liquor must not be titrated directly with iodine, but an excess must be added, and the excess of iodine titrated back with thiosulphate and starch. In another equal volume the sulphuretted hydrogen is determined by the method given above, the number of cubic centimetres of iodine required being denoted by B. A further equal volume is then mixed with an ammoniacal solution of zinc and strontium chlorides, the former removing the sulphide and the latter

the sulphite. The filtrate contains the thiosulphate and is titrated with iodine as before, the number of cubic centimetres of iodine required being denoted by C. The following data are thus obtained in terms of the iodine solution:—

Sulphide	=	B
Thiosulphate	=	C
Sulphite	=	A - (B + C).

The figures for sulphite and especially for thiosulphate are probably only very approximate, owing to the fact that the organic matter present in the liquor materially affects the quantity of iodine used both in the titration of the original liquor, and in that of the liquor after removal of the sulphide and sulphite.

**6. Total Sulphur.**—Fifty c.c. of liquor (100 c.c. if dilute) are slowly dropped into a flask containing an excess of bromine free from sulphur, covered with water moderately acidified with hydrochloric acid, the flask being constantly shaken during the addition. The oxidised solution is evaporated to dryness on the water-bath, the residue extracted with water, made up to 250 c.c., and 100 c.c. precipitated as barium sulphate, which is filtered off, dried, and weighed.

$$\text{Grams sulphur per 100 c.c.} = 5 \times 0.1374 \times \text{g. BaSO}_4.$$

Certain liquors, especially from coke ovens and blast furnaces, yield a heavy precipitate of brominated phenols, which retain traces of sulphate. This is recovered by fusing the residue insoluble in water with as small a quantity as possible of potassium carbonate and nitrate, or of sodium peroxide, and subsequent precipitation with barium chloride.

**7. Thiocyanate.**—1. *Ferrocyanide absent.* Fifty c.c. of liquor are treated with lead carbonate to remove sulphide, the lead sulphide and excess of lead carbonate filtered off and washed, the filtrate treated with sodium sulphite containing sulphurous acid, so that it is just acid, warmed, an excess of 10 per cent. copper sulphate solution added, and the whole digested at 70° to 80° for five to ten minutes. The precipitated cuprous thiocyanate is filtered off, washed free from copper solution, the filter paper and precipitate then transferred to the beaker or flask used for the precipitation, and digested at 30° to 40° with 25 c.c. of 4 per cent. sodium hydroxide free from chloride. After filtering off and washing the cuprous hydroxide formed, the cold filtrate is acidified with dilute nitric acid free from oxides of nitrogen, filtered if necessary, and titrated with *N*/10 silver nitrate, using iron alum as indicator (*cf.* also p. 677).

$$\begin{aligned} 1 \text{ c.c. } N/10 \text{ AgNO}_3 &= 0.007612 \text{ g. NH}_4\text{CNS} \\ &= 0.002702 \text{ g. HCN} \\ &= 0.003207 \text{ g. S.} \end{aligned}$$



2. *Ferrocyanide present.* Fifty c.c. of liquor are made just acid by sulphuric acid, ferric alum solution added till the solution is strongly coloured by ferric thiocyanate, the solution warmed to  $60^{\circ}$ , filtered from precipitated Prussian blue through a folded filter, and the precipitate washed with water containing sodium or ammonium sulphate; the filtrate is then treated as above.

8. *Hydrocyanic Acid.*—For this estimation Feld's method is employed. Fifty c.c. of the liquor are diluted to about 250 c.c. in a large flask, a solution of about 5 g. of lead nitrate added, and the whole distilled for 20 to 30 minutes, the steam evolved being condensed and collected in 25 c.c. of  $N/1$  sodium hydroxide in a receiver, the end of the condenser dipping below the surface of the liquid. The cyanogen present in the form of cyanide distils over as hydrocyanic acid and is converted into sodium cyanide in the receiver, its amount being estimated by diluting the distillate to 400 c.c., adding a crystal of potassium iodide and titrating with  $N/10$  silver nitrate until a permanent precipitate of silver iodide is formed.

Grams HCN per 100 c.c. =  $2 \times 0.005403 \times \text{c.c. } N/10 \text{ AgNO}_3$ .

In some cases the liquid froths up considerably during distillation, and it is, therefore, advisable to use a flask of large capacity and to heat cautiously at first.

9. *Ferrocyanic Acid.*—Feld's method is also employed for this determination. Two hundred and fifty c.c. of the liquor is made just acid with sulphuric acid, ferric alum solution added till the solution is strongly coloured by ferric thiocyanate, and the whole warmed to  $60^{\circ}$ . The precipitated Prussian blue is then filtered through a folded filter, which usually retains it completely. If, however, some passes through, the filtrate is returned to the filter until a small portion shows no blue colour when the ferric thiocyanate coloration is destroyed by mercuric chloride; the precipitate is washed with water containing sodium or ammonium sulphate. The filter and precipitate are then transferred to a flask and boiled for five minutes with 10 c.c. of  $N/1$  sodium hydroxide and analysed by the Feld method as described on p. 729.

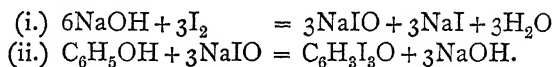
$$\begin{aligned} 1 \text{ c.c. } N/10 \text{ AgNO}_3 &= 0.00947 \text{ g. } (\text{NH}_4)_4\text{Fe}(\text{CN})_6 \\ &= 0.00714 \text{ g. } \text{H}_4\text{Fe}(\text{CN})_6. \end{aligned}$$

10. *Phenols.*—For the estimation of the amount of phenols in ammoniacal liquor, the most suitable method is that of Skirrow,<sup>1</sup> which depends on the isolation of these compounds, by distillation of the acidified liquor with steam, and treatment of the distillate with an excess of standard iodine solution and titrating back with sodium thio-sulphate according to the method of Messinger and Vortmann.<sup>2</sup>

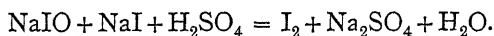
<sup>1</sup> *J. Soc. Chem. Ind.*, 1908, 27, 58.

<sup>2</sup> *Ber.*, 1889, 22, 2313; Cf. also Korn, *Z. anal. Chem.*, 1906, 45, 552.

The treatment with iodine takes place in alkaline solution, the reactions being as follows :—



Each molecule of phenol (or its homologues), therefore, effects the conversion of six atoms of iodine into tri-iodophenol and sodium iodide, and the excess, above this proportion, forms a mixture of sodium hypoiodite and iodide with the alkali, which on addition of acid is converted into free iodine, and may be estimated with sodium thio-sulphate :—



To carry out the estimation, 100 c.c. of liquor are treated with ammonium polysulphide solution to convert any cyanide into thiocyanate, and diluted, after standing, to 200 c.c., and the sulphuretted hydrogen removed by treatment with lead carbonate and filtration through a dry filter. An excess of sodium hydroxide (25 c.c. of a 50 per cent. solution) is added to 100 c.c. of the filtrate (= 50 c.c. of original liquor), and the liquid evaporated until separation of salts takes place; the residue is washed into a distilling flask, diluted to about 150 c.c., and when cold, acidified with sulphuric acid. The liquid is then distilled until salts separate, yielding "distillate 1"; 100 c.c. of water are added to the distilling flask, again distilled forming "distillate 2," and the operation again repeated yielding "distillate 3." Each distillate is treated with 1 g. of precipitated calcium carbonate and a little lead carbonate to remove acid and sulphuretted hydrogen, and again distilled, "distillate 1" being distilled first, No. 2 then added to the distilling flask and distilled, and finally No. 3 distillate in the same manner. The combined distillates, which consist of a pure solution of the phenols contained in the liquor, are then made up to 500 c.c.

Fifty c.c. of this solution (= 10 c.c. of original liquor) is made slightly alkaline with sodium hydroxide, warmed to 60°, an excess of *N*/10 iodine solution added, the flask stoppered, and allowed to cool with frequent shaking; the liquid is then acidified and titrated with *N*/10 sodium thiosulphate, using starch as indicator, the end-point of the reaction being indicated by a transition of colour from blue to rose pink.

Each cubic centimetre of iodine used corresponds to 0.001567 g. of phenol; the number of grams of phenol per 100 c.c. of liquor, if the above quantities are taken, is therefore :—

$$10 \times 0.001567 \times \text{c.c. of iodine used}.$$

An excess of alkali makes the end-point of the reaction less sharp; it is, therefore, advisable to make a first titration, using 2 c.c. of *N*/1

sodium hydroxide, and then to make a second titration in which 4 gram-molecules of sodium hydroxide are present for each gram-molecule of phenol found in the first experiment.

The phenols present are all calculated as phenol itself,  $C_6H_5OH$ , but as a matter of fact some 35 per cent. of the whole consists of higher homologues, chiefly cresols; as the latter combine with a smaller proportion of iodine than phenol, the results obtained are rather low.

For a quick, approximate estimation of the phenols in ammoniacal liquor, White and Clary<sup>1</sup> acidify 1 litre of the liquor with concentrated hydrochloric acid, extract with 100 c.c. of chloroform by shaking in a separating funnel, and evaporate the chloroform extract in a flask. The weight of residual phenols amounts approximately, under these conditions, to one quarter of the total amount present.

## IX.—LIQUOR AMMONIÆ AND LIQUEFIED AMMONIA

### A. MANUFACTURE

In the manufacture of pure ammonia solution or of the liquefied gas, the whole of the acid constituents present in the gas liquor must be removed by alkali. Lime is almost always employed for this purpose on account of its cheapness, a sufficient amount being added to the liquor before distillation to combine with these acids including the whole of the carbon dioxide and sulphuretted hydrogen; or, if only sufficient lime be added to decompose the fixed ammonium salts, the gas evolved is freed from these gases by washing with hot milk of lime, to which, in some cases, ferrous or ferric sulphate is added, the resulting iron hydroxide effecting the complete removal of sulphuretted hydrogen.

In order to economise lime, the liquor is often first heated without any addition of lime, when a large proportion of the sulphuretted hydrogen and carbon dioxide is evolved, accompanied by only a small proportion of ammonia; the latter is removed by washing the gases with weak liquor or water, or, if the manufacture of liquor ammoniæ be combined with that of the sulphate, by allowing the gas to pass through the sulphuric acid in the saturator of the plant employed for the latter purpose.

**Valuation of the Lime.**—The methods of analysis are fully described in Vol. I., p. 483. The figures thus obtained for the percentage of lime, do not, however, always represent correctly the true relative value of a sample for this particular purpose as some particles of the latter may not be obtained in a sufficiently, finely divided state on

<sup>1</sup> *J. Gas Lighting*, 1905, 92, 467.

slaking, or may become covered with a layer of calcium carbonate, and thus act very slowly, if at all. On this account, an excess of lime above that theoretically required is always employed.

Pfeiffer<sup>1</sup> estimates the amount of active lime present in the following manner:—A large average sample is broken to the size of beans, and then further crushed and sampled in the laboratory. Seventy grams of the product is poured into 750 c.c. of boiling water in an enamelled saucepan provided with a cover, and, after slaking, made up to a litre. Twenty c.c. of the well-shaken cream are then withdrawn by a pipette having a wide delivery tube, and quickly titrated with *N*/1 hydrochloric acid, using phenolphthalein as indicator, until the red colour disappears; the hydrochloric acid used represents the active lime present. The less active lime slowly dissolves, and the red colour reappears; quantities of 0.5 c.c. of acid are then added successively, until no reappearance of the red colour occurs after an interval of five minutes; the additional quantity of acid used represents the less active lime. The older the lime, the greater is the quantity of less active lime found.

The amount of lime required for any sample of liquor may be found from a determination of the amounts of fixed ammonia, carbon dioxide, and sulphuretted hydrogen contained in it, and calculating the amount of lime therefrom, in accordance with the following figures.

Each 17 parts of fixed ammonia require	28 parts of lime.
„ 22 „ CO <sub>2</sub> . . „	28 „ „
„ 34 „ H <sub>2</sub> S . . „	56 „ „

The amount may be found more conveniently by boiling 25 to 50 c.c. of gas liquor (or 100 c.c. of heated liquor) with 40 c.c. of milk of lime, prepared in the manner described above, until no more ammonia is evolved, allowing to cool, adding phenolphthalein, and titrating with *N*/1 hydrochloric acid until the red coloration disappears. Each cubic centimetre of *N*/1 HCl = 0.02805 g. CaO. The acid thus required corresponds to the unaltered excess of lime; the difference between this and the amount of lime taken, estimated by direct titration of a further 40 c.c. of the milk of lime with *N*/1 acid, gives the quantity of lime theoretically required for the volume of liquor taken.

## B. PURE AMMONIA

**1. Strength of Solution.**—This is usually estimated from the specific gravity by the Table given on p. 742, but may also be determined by titration with standard acid. The strongest ammonia sold commercially has a sp. gr. of about 0.880; it contains 36 per cent. of ammonia, and is sold as “0.880” ammonia.

**2. Inorganic Impurities.**—These comprise sulphuretted hydrogen

<sup>1</sup> *J. Gasbeleucht.*, 1898, 41, 69, 113; 1900, 43, 89; 1903, 46, 1.

and carbon dioxide, if too little lime has been used for the distillation ; chlorine and lime, which find their way from the condenser water to the pure water in the absorption vessels in case of leakages in the apparatus, and traces of iron and copper. These are tested for qualitatively with the following reagents in succession :—Ammoniacal lead acetate solution, calcium chloride, mixture of acetic acid and silver nitrate, oxalic acid, ammonium sulphide, and ammonium thiocyanate. Commercial ammonia should be free from these impurities.

Specific Gravities of Ammonia Solutions at 15° C.<sup>1</sup>

Sp. gr. at 15°.	Per cent. NH <sub>3</sub> .	1 litre contains NH <sub>3</sub> at 15° g.	Correction of the sp. gr. for $\pm 1^\circ$ .	Sp. gr. at 15°.	Per cent. NH <sub>3</sub> .	1 litre contains NH <sub>3</sub> at 15° g.	Correction of the sp. gr. for $\pm 1^\circ$ .
1.000	0.00	0.0	0.00018	0.940	15.63	146.9	0.00039
0.998	0.45	4.5	0.00018	0.938	16.22	152.1	0.00040
0.996	0.91	9.1	0.00019	0.936	16.82	157.4	0.00041
0.994	1.37	13.6	0.00019	0.934	17.42	162.7	0.00041
0.992	1.84	18.2	0.00020	0.932	18.03	168.1	0.00042
0.990	2.31	22.9	0.00020	0.930	18.64	173.4	0.00042
0.988	2.80	27.7	0.00021	0.928	19.25	178.6	0.00043
0.986	3.30	32.5	0.00021	0.926	19.87	184.2	0.00044
0.984	3.80	37.4	0.00022	0.924	20.49	189.3	0.00045
0.982	4.30	42.2	0.00022	0.922	21.12	194.7	0.00046
0.980	4.80	47.0	0.00023	0.920	21.75	200.1	0.00047
0.978	5.30	51.8	0.00023	0.918	22.39	205.6	0.00048
0.976	5.80	56.6	0.00024	0.916	23.03	210.9	0.00049
0.974	6.30	61.4	0.00024	0.914	23.68	216.3	0.00050
0.972	6.80	66.1	0.00025	0.912	24.33	221.9	0.00051
0.970	7.31	70.9	0.00025	0.910	24.99	227.4	0.00052
0.968	7.82	75.7	0.00026	0.908	25.65	232.9	0.00053
0.966	8.33	80.5	0.00026	0.906	26.31	238.3	0.00054
0.964	8.84	85.2	0.00027	0.904	26.98	243.9	0.00055
0.962	9.35	89.9	0.00028	0.902	27.65	249.4	0.00056
0.960	9.91	95.1	0.00029	0.900	28.33	255.0	0.00057
0.958	10.47	100.3	0.00030	0.898	29.01	260.5	0.00058
0.956	11.03	105.4	0.00031	0.896	29.69	266.0	0.00059
0.954	11.60	110.7	0.00032	0.894	30.37	271.5	0.00060
0.952	12.17	115.9	0.00033	0.892	31.05	277.0	0.00060
0.950	12.74	121.0	0.00034	0.890	31.75	282.6	0.00061
0.948	13.31	126.2	0.00035	0.888	32.50	288.6	0.00062
0.946	13.88	131.3	0.00036	0.886	33.25	294.6	0.00063
0.944	14.46	136.5	0.00037	0.884	34.10	301.4	0.00064
0.942	15.04	141.7	0.00038	0.882	34.95	308.3	0.00065

**3. Empyreumatic Ingredients.**—Ammonia solutions are seldom completely free from compounds of a pyridine nature which impart to it an unpleasant odour and which are also regarded as the cause of the occasional darkening of the originally clear solution. As soon as they show their presence to a large extent, the carbon filter employed for the removal of those empyreumatic constituents from the gas as evolved from the still must be renewed. Frequent testing of the solution is desirable from this point of view.

<sup>1</sup> Lunge & Wiernik, *Z. angew. Chem.*, 1889, 2, 181.

By dipping a piece of filter paper in the ammonia to be examined the empyreumatic odour may be perceived after the ammonia has volatilised, but in a short time the former also disappears. The odour is more readily perceptible if a small sample of the liquid is neutralised with sulphuric acid. Pfeiffer adds litmus tincture to the sample, slightly acidifies it, and then throws a little precipitated calcium carbonate into the liquid to take up the excess of acid.

According to Wittstein,<sup>1</sup> tarry matters or organic bases in ammonia solution are detected by adding, drop by drop, nitric acid diluted with one-quarter of its volume of water; a rose coloration is produced which, however, disappears again if the addition of the acid be continued until the liquid is neutral.

For the quantitative estimation of pyridine, Pennock and Morton<sup>2</sup> proceed as follows:—One hundred c.c. of the sample are nearly neutralised with sulphuric acid (1:5), and after cooling, made exactly neutral with normal sulphuric acid, using one to two drops of methyl orange as indicator. The neutralised liquid is distilled into a receiver containing 30 c.c. of water until 70 c.c. have distilled over; the whole of the pyridine is then contained in the distillate, if the amount does not exceed 2.5 g. per litre. The distillate, cooled to 10°, is then mixed with phenolphthalein, which gives a red coloration with ammonia, but not with pyridine. Ammonia is removed as "white precipitate" by adding mercuric chloride till the solution is decolorised, followed by an additional four drops of the mercuric chloride solution after decolorisation, and the filtered liquid titrated with *N*/10 sulphuric acid and methyl orange. One c.c. *N*/10 acid = 0.0079 g. pyridine.

### C. LIQUEFIED AMMONIA

The liquid ammonia, which is supplied commercially in steel cylinders under pressure as liquefied ammonia, and which is chiefly used in the manufacture of ice, is by no means a pure chemical product. It generally contains small quantities of water and organic substances which have been identified by Lange and Hertz<sup>3</sup> as consisting mainly of pyridine, acetonitrile, ethyl alcohol, and a little machine oil. The presence of these impurities, which may amount to about 2 per cent., is under certain circumstances detrimental to the use of liquid ammonia, and it is, therefore, of importance to determine them analytically, or at any rate to estimate their total amount. The ordinary determinations of the concentration, as made in testing ammonia solutions, are, of course, not applicable. The usual procedure is to allow a sample of the liquefied gas to evaporate spontaneously under specified conditions,

<sup>1</sup> *Dingl. polyt. J.*, 1874, 213, 512.

<sup>2</sup> *J. Amer. Chem. Soc.*, 1902, 24, 377.

<sup>3</sup> *Z. angew. Chem.*, 1897, 10, 224.

and to determine the non-gaseous residue either gravimetrically or volumetrically.

(i.) Bunte and Eitner<sup>1</sup> have recommended a method of sampling by which any impurities due to condensation of the moisture of the air is excluded. A pipette, P (Fig. 118), of about 75 c.c. capacity, provided with two stopcocks, serves for the reception of the liquefied ammonia, the inlet tube of which terminates in a smoothly ground ring. The cylinder B, containing the ammonia to be examined, is placed with the valve downwards and the side tube connected by a union with a thin brass tube, the end of which is formed into a flange; the ground ring of the pipette is held against the flange by means of the clamp Z, a leather washer being inserted between the two surfaces. The sample is passed over from the cylinder to the pipette with the latter in a horizontal position, by first opening the valve and, after driving out the air, closing the outer stopcock of the pipette. When about two-thirds of the

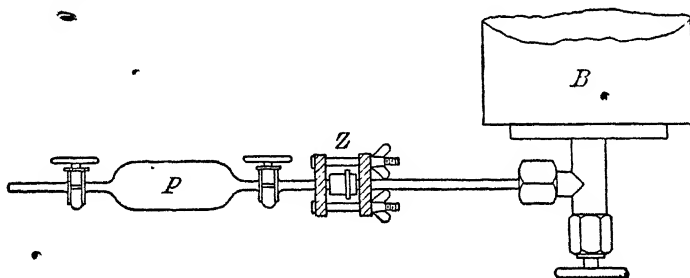


FIG. 118.

pipette are filled with liquid ammonia, the valve and the second stopcock of the pipette are closed and the pipette then removed; the increase in weight of the pipette is then determined. The pipette is next placed in an upright position, connected to a series of three tared drying tubes, filled with potassium hydroxide, and the upper stopcock opened carefully, so that a slow current of gas passes through the tubes by the evaporation of the ammonia, the stream being regulated by a mercury seal at the outlet. After the lapse of from four to six hours, evaporation ceases, and there remain in the pipette a few drops of a brown liquid which consists partly of water saturated with ammonia, partly of organic compounds resembling alcohols, and hydrocarbons coloured with traces of tarry constituents. The pipette is then warmed in an air-bath to 70° to 80°, whilst a current of dry air is passed through; the volatile organic compounds, as well as the water, are thus driven over into the potash tubes; any trace of organic matter remaining behind is weighed as such together with the pipette. The total quantity of volatile organic matter and water is ascertained from the increase in weight of the potash tube.

<sup>1</sup> *J. Gasbeleucht.*, 1897, 40, 1748

The following results were, for example, obtained by this method :— High boiling organic substances = 0.08 per cent.; volatile alcohols and water = 0.41 per cent.; total impurities, therefore, = 0.49 per cent.

For the purpose of testing deliveries of liquid ammonia, the following simplified method, due to Lange and Hertz,<sup>1</sup> is commonly employed. To a glass tube 30 to 40 mm. in width, a narrow tube of about 5 mm. in width is fused, which is closed at the lower end (Fig. 119); the total capacity of the tube is about 80 to 100 c.c. A mark is placed on the tube corresponding to a content of 49 c.c. = 33 g. of liquid ammonia, and the narrow portion is graduated into fifteen divisions, the total volume of the fifteen divisions being 1 c.c.; each of these divisions corresponds to 0.2 per cent. by volume, on the assumption that the specific gravity of liquid ammonia is 0.68 at  $-38^{\circ}$ , and that of the residue 0.9 at  $15^{\circ}$ . To take a sample, the ammonia cylinder is placed in a horizontal position, the valve opened slightly, and the liquid allowed to flow into the tube until it reaches the 49 c.c. mark. The liquid is then allowed to evaporate spontaneously, which requires about three hours, a cork and glass tube being placed if desired at the top of the tube, and the evolved ammonia led into water. As soon as evaporation is complete and the ice layer which forms on the outside of the tube has thawed, the volume of residue is read off. The method is naturally only an approximate one, and tends to give rather too high results, as some ammonia evaporates during the taking of the sample, the high boiling impurities tend to accumulate in the sample actually measured, and the residue always contains ammonia. These errors are partly compensated for, owing to the fact that some of the less volatile impurities evaporate with the ammonia, and the results are accordingly sufficiently accurate for most purposes.



FIG. 119.

## X.—AMMONIUM SALTS

The only ammonium salt usually manufactured in gasworks is the sulphate; this salt is employed to much the greatest extent in commerce, chiefly for manurial purposes. Other salts are, for the most part, manufactured in chemical works from ammoniacal liquor purchased from Gas or Coke-oven Undertakings; the most common of these are the chloride, nitrate, carbonate, and thiocyanate (sulphocyanide).

In the manufacture of ammonium sulphate, the volatile ammonia is in the first instance distilled off, lime being only added after this has been removed, the quantity required being then only a working excess

<sup>1</sup> *Z. angew. Chem.*, 1897, 10, 224.



over the amount corresponding to the fixed ammonium salts present. The mixture of ammonia, steam, carbon dioxide, sulphuretted hydrogen, hydrocyanic acid, and other impurities, is passed through a saturator charged with sulphuric acid, whereby the ammonia is retained and converted into sulphate, the crystals of which separate when sufficient concentration is reached and are removed by perforated ladles. The remaining gases pass through the saturator, and, after cooling, are treated for the removal of the sulphuretted hydrogen and hydrocyanic acid, the plan most commonly adopted being to allow them to pass through a purifier containing hydrated oxide of iron before escaping into the atmosphere.

The analysis of the waste liquor from the stills is carried out by the methods described for the gas liquor, modified, in the case of the determination of ammonia, by increasing the volume taken for analysis and employing decinormal in place of normal solutions.

For the analysis of the waste gases, methods are given by Linder,<sup>1</sup> in which the amounts of sulphuretted hydrogen, carbon dioxide, and hydrocyanic acid are estimated in a manner analogous to that employed for these constituents in ammoniacal liquids.

#### THE ANALYSIS OF AMMONIUM SALTS

In the case of the commercial sulphate used for manurial purposes, the only determination usually made is the percentage of ammonia, on which its value depends. Formerly, when sulphate was frequently made by the direct neutralisation of gas liquor with sulphuric acid, very impure products were sometimes sold containing thiocyanate, but such products are now rarely, if ever, met with. With the carbonate also only the ammonia is usually determined. In some cases, such as the nitrate, when used for the manufacture of explosives, the percentage of the acid constituent may be required.

For the complete analysis and for the determination of general or special impurities, 40 g. of the salt are dissolved in water, filtered through a dried, tared filter paper, and, after washing the latter with water, made up to 1 litre. The insoluble residue is dried and weighed, and the percentage of insoluble matter calculated from the nett weight of the precipitate. The solution is then employed for the determination of the soluble constituents, each 25 c.c. being equal to 1 g. of the original salt.

**1. Ammonium Sulphate.**—The salt supplied commercially is nearly always moist, usually still somewhat acid, and slightly coloured by traces of organic bases.

*Moisture.* Five grams of the salt are heated in an air-bath for two hours at 110°; the loss of weight gives the percentage of moisture.

<sup>1</sup> *Report on Alkali, etc., Works*, 1906, p. 52.

*Ammonia.* This estimation is carried out by distilling 25 c.c. of the solution prepared as above (=1 g. salt) with sodium hydroxide, and collecting the distillate in 25 c.c. of standard sulphuric acid, in the manner described under gas liquor. Each cubic centimetre of  $N/1$  acid neutralised = 0.01401 g.  $N$  or 0.1703 g.  $NH_3$ .

The determination of ammonia by the azotometer (*cf.* Vol. I., p. 125) may also be used, but for exact results the distillation method is preferable.

#### Percentage content of Solutions at 15° C.<sup>1</sup>

Per cent.	Sp. gr.	Per cent.	Sp. gr.	Per cent.	Sp. gr.	Per cent.	Sp. gr.
1	1.0057	14	1.0805	27	1.1554	40	1.2284
2	1.0115	15	1.0862	28	1.1612	41	1.2343
3	1.0172	16	1.0920	29	1.1670	42	1.2402
4	1.0230	17	1.0977	30	1.1724	43	1.2462
5	1.0287	18	1.1035	31	1.1780	44	1.2522
6	1.0345	19	1.1092	32	1.1836	45	1.2583
7	1.0403	20	1.1149	33	1.1892	46	1.2644
8	1.0460	21	1.1207	34	1.1948	47	1.2705
9	1.0518	22	1.1265	35	1.2004	48	1.2766
10	1.0575	23	1.1323	36	1.2060	49	1.2828
11	1.0632	24	1.1381	37	1.2116	50	1.2890
12	1.0690	25	1.1439	38	1.2172		
13	1.0747	26	1.1496	39	1.2228		

*Total Sulphuric Acid.* Twenty-five c.c. of the solution are diluted, and precipitated with barium chloride in boiling solution in the usual manner. The weight of barium sulphate, multiplied by 0.343, gives the weight of  $SO_3$  in 1 g. of the salt.

*Free Sulphuric Acid.* Twenty-five c.c. of the solution are titrated with  $N/10$  sodium hydroxide, using methyl orange as indicator. Each cubic centimetre of  $N/10$  acid = 0.0049 g.  $H_2SO_4$ .

*Residue on Ignition.* Two grams of the salt are carefully volatilised in a covered platinum crucible and the residue weighed.

**2. Ammonium Chloride (*Sal Ammoniac*).**—*Percentage Content of Solutions at 15°.* The following table gives the strengths of solutions of different specific gravities, according to Gerlach, and Lunge and Kohler.<sup>2</sup>

Per cent. $NH_4Cl$ .	Sp. gr.	Per cent. $NH_4Cl$ .	Sp. gr.	Per cent. $NH_4Cl$ .	Sp. gr.	Per cent. $NH_4Cl$ .	Sp. gr.
1	1.00816	8	1.02481	15	1.04524	22	1.06479
2	1.00632	9	1.02781	16	1.04804	23	1.06754
3	1.00948	10	1.03081	17	1.05086	24	1.07029
4	1.01264	11	1.03370	18	1.05367	25	1.07304
5	1.01580	12	1.03658	19	1.05648	26	1.07575
6	1.01880	13	1.03947	20	1.05929		
7	1.02180	14	1.04225	21	1.06204		

<sup>1</sup> Lunge, *Coal Tar and Ammonia*, 4th edition, 1909, p. 959.

<sup>2</sup> *Ibid.*, p. 958.

The percentages of ammonia, moisture, free acid, insoluble matter, and residue on ignition are estimated in the same manner as with the sulphate.

*Chlorine.* This is most readily determined by titrating 5 c.c. of the solution (40 g. per litre) with neutral  $N/10$  silver nitrate, using potassium chromate as indicator. Each cubic centimetre of  $N/10$  silver nitrate = 0.003546 g. Cl.

*Iron.* This impurity is sometimes present in commercial sal-ammoniac, spoiling its appearance, and being also detrimental to its employment in the colour industry. Its amount may be ascertained by titration with  $N/10$  bichromate, after reduction of the iron to the ferrous state by any of the usual methods.

**3. Ammonium Carbonate.**—Commercial ammonium carbonate is a mixture of ammonium carbamate,  $\text{NH}_2\text{CO.ONH}_4$ , and ammonium bicarbonate,  $\text{NH}_4\text{HCO}_3$ ; it effloresces in the air, losing ammonia, carbon dioxide, and water, and leaving a residue of ammonium bicarbonate. It is usually manufactured by heating a mixture of calcium carbonate and ammonium sulphate, the mixture of ammonia, carbon dioxide, and moisture condensing as a solid crust in cooling chambers. The commercial product, when fresh, usually contains about 30 per cent. of ammonia.

*Percentage Content of Solutions at 15°.* The following table, due to Lunge and Smith,<sup>1</sup> gives the specific gravity of solutions of commercial carbonate, the dry salt having the following composition:—

Ammonia	.	.	.	.	31.3 per cent.
Carbon dioxide	.	.	.	.	56.6 "
Water	.	.	.	.	12.1 "

Degrees Twaddel.	Sp. gr. at 15°.	Per cent. of Ammonium Carbonate.	Alteration of sp. gr. for $\pm 1^\circ$ .	Degrees Twaddel.	Sp. gr. at 15°.	Per cent. of Ammonium Carbonate.	Alteration of sp. gr. for $\pm 1^\circ$ .
1	1.005	1.66	0.0002	15	1.075	22.25	0.0006
2	1.010	3.18	0.0002	16	1.080	23.78	0.0006
3	1.015	4.60	0.0003	17	1.085	25.31	0.0007
4	1.020	6.04	0.0003	18	1.090	26.82	0.0007
5	1.025	7.49	0.0003	19	1.095	28.33	0.0007
6	1.030	8.93	0.0004	20	1.100	29.93	0.0007
7	1.035	10.35	0.0004	21	1.105	31.77	0.0007
8	1.040	11.86	0.0004	22	1.110	33.45	0.0007
9	1.045	13.36	0.0005	23	1.115	35.08	0.0007
10	1.050	14.88	0.0005	24	1.120	36.88	0.0007
11	1.055	16.16	0.0005	25	1.125	38.71	0.0007
12	1.060	17.70	0.0005	26	1.130	40.34	0.0007
13	1.065	19.18	0.0005	27	1.135	42.20	0.0007
14	1.070	20.70	0.0005	28	1.140	44.29	0.0007

Insoluble matter and the residue on ignition may be determined as in the case of the sulphate. The ammonia may also be estimated by

<sup>1</sup> *J. Soc. Chem. Ind.*, 1883, 2, 80.

distillation in the usual manner, or the solution may be titrated directly with normal acid, using methyl orange as indicator.

**4. Ammonium Nitrate.**—In addition to ammonia, the estimation of the nitric acid and of the nitrous acid, frequently present in the commercial salt, may be required.

*Nitric acid* is estimated as described in Vol. I., pp. 311 *et seq.*, the methods most frequently employed being those of Ulsch, Schlösing-Grandeau, and Lunge.

*Nitrous acid* is estimated qualitatively in the manner described in Vol. I., p. 759; when present in only small amount, colorimetric methods are used (Vol. I., p. 761). If the quantity is too large for colorimetric estimation, which is seldom the case, the nitrous acid is determined by titration with potassium permanganate.

**5. Ammonium Thiocyanate** (*Sulphocyanide*).—This salt is now rarely recovered from spent oxide, but is obtained directly from the crude coal gas by treatment with ammonium polysulphide solution (*cf.* p. 675), or synthetically by the combination of carbon bisulphide with ammonium sulphide, and conversion of the thiocarbonate formed into thiocyanate.

The amount of ammonia in the salt is estimated by distillation with sodium hydroxide, and the thiocyanic acid by titrating the solution, acidified with nitric acid, with *N/10* silver nitrate, using ferric alum as indicator, with previous precipitation as cuprous thiocyanate if chloride, thiosulphite, etc., are present.

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# COAL TAR

By Dr H. KÖHLER, Berlin. English translation revised by Prof. A. G. GREEN, M.Sc., Professor of Technical Chemistry, The University, Leeds.

## A. RAW MATERIALS

The available sources of coal tar are :—

1. *The Coal Gas Industry*, which still supplies, under the name of "gas tar," the greater portion of the coal tar which is used in England.
2. *The Coke Industry*, which also produces very considerable quantities of tar, known as "coke oven tar." This source of supply has become important since the introduction of closed coke ovens, and it may be expected that in course of time it may exceed that from the coal gas industry.
3. *The Pig Iron Industry*, in which the recovery of the volatile products of the blast furnace has been successfully carried out, especially in Scotland, with the result that quite considerable quantities of a peculiar tar, known as "blast furnace tar," are now placed on the market.
4. *The Generator and Water Gas Industries*, which are of special importance in England and America. The liquid by-product which is obtained comes into the market as "Producer tar" or "Water gas tar."
5. *The Oil Gas Industry*, in which tar is produced as the result of the pyrogenetic decomposition of oils and petroleum residues.

## I.—PROPERTIES AND COMPOSITION OF COAL TAR

Coal tar is of a dark colour, usually black, its consistency oily or viscous, and its odour characteristic, and similar to that of creosote; this last varies, however, according to its origin. Its physical properties and chemical composition are largely dependent on the nature of the original coal, and still more on the method of production. The viscosity of coal tar results from the presence of solid hydrocarbons (naphthalene, phenanthrene, etc.), and so-called "free carbon" (soot); the latter is also the cause of its dark colour.

The specific gravity of coal tar from various sources lies within rather wide limits, as is shown in the following table :—

Source of the Coal Tar.	Specific Gravity.		
	From	To	Average.
Gas tar (horizontal and inclined retorts) <sup>1</sup>	1.115	1.220	1.155
Gas tar (Bueb's vertical retorts) <sup>2</sup>	1.110	...	1.110
Coke oven tar:—			
(a) From Simon-Carvès oven <sup>3</sup>	1.106	1.150	1.110
(b) From Carvès-Hüssener oven <sup>4</sup>	1.139	...	...
(c) From Hoffmann-Otto oven <sup>5</sup>	1.1198	...	...
(d) From Semet-Solvay oven <sup>6</sup>	1.170	...	...
(e) From Jameson oven <sup>7</sup>	0.960	0.994	0.977
Blast furnace tar <sup>8</sup>	0.954	...	...
Producer tar <sup>9</sup>	1.080	...	...
Water gas tar <sup>10</sup>	1.100	...	...
Oil gas tar <sup>11</sup>	0.950	1.000	0.975

The specific gravity of coal tar depends on the nature of its constituents, and, in the case of gas tar, mainly on the proportion of free carbon.<sup>12</sup>

Coal tars with a specific gravity of less than 1.0 usually consist mainly of hydrocarbons of the aliphatic series, whereas those of higher specific gravity consist essentially of aromatic hydrocarbons. These differences are a function of the temperature at which the carbonisation of the coal is effected.<sup>13</sup>

Tars lighter than water are only obtained in exceptional cases, for instance, from the Jameson coke ovens and from blast furnace gases, and are worked up in a special manner. Only the heavier tars come under the category of what is usually termed "coal tar."

The following elementary analyses of coal tar are given by E. Mills:<sup>14</sup>—

	London Gas Tar.	Tar from Scotch Cannel.
	Per cent.	Per cent.
Carbon . . . . .	77.53	85.33
Hydrogen . . . . .	6.33	7.33
Nitrogen . . . . .	1.03	0.85
Sulphur . . . . .	0.61	0.43
Oxygen . . . . .	14.50	6.06
	100.00	100.00

Coal tar differs from wood tar in consisting mainly of aromatic hydrocarbons, whilst the latter contains chiefly phenolic deriva-

<sup>1</sup> H. Köhler, *Dingl. polyt. J.*, 1888, 270, 233.

<sup>2</sup> *J. Gasbeleucht.*, 1906, 49, 955.

<sup>3</sup> Watson Smith, *J. Soc. Chem. Ind.*, 1884, 3, 605.

<sup>4</sup> A. Hüssener, *Stahl u. Eisen*, 1883, 4, 397.

<sup>5</sup> Lunge and Schmid, *Chem. Ind.*, 1887, 10, 337.

<sup>6</sup> H. O. Hoffmann, *Eng. and Min. J.*, 1898, p. 428.

<sup>7</sup> Watson Smith, *J. Soc. Chem. Ind.*, 1883, 2, 403.

<sup>8</sup> *Ibid.*

<sup>9</sup> *Ibid.*

<sup>10</sup> *Amer. Chem. J.*, 1884, 6, 77.

<sup>11</sup> Scheithauer, *Braunkohlenteerproducte u. Ölgas*, p. 147.

<sup>12</sup> Köhler, *Dingl. polyt. J.*, 1888, 270, 233.

<sup>13</sup> Cf. Lunge, *Coal Tar and Ammonia*, 4th ed., 1909, pp. 16 et seq.

<sup>14</sup> *J. Soc. Chem. Ind.*, 1885, 4, 326.

tives. Tar from peat, lignite, and bituminous shales is principally composed of hydrocarbons of the aliphatic series. Numerous substances have been discovered in coal tar, but much still remains unknown with respect to the composition of pitch, anthracene oil, etc. Coal tar also invariably contains a considerable quantity of ammonia water mechanically mixed with it, and, therefore, also contains the constituents of the latter, and in addition those of illuminating gas, which are physically absorbed.

## II.—CHARACTERISTICS OF TARs

### (a) Gas Tar.

The great changes due to the introduction of vertical retorts and of chamber retorts in the manufacture of illuminating gas will have a considerable influence on the quality of the tar, which must be taken into account in judging its value.

B. Nickels<sup>1</sup> gives the following figures for the average composition of London and English country tars:—

	London.	Country.
	Per cent.	Per cent.
Ammoniacal Water . . . . .	4.5	4.0
Light Oil . . . . .	2.4	3.0
Carbolic and Cresote Oils . . . . .	20.3	22.0
Anthracene Oil . . . . .	15.0	4.0
Pitch . . . . .	58.0	67.0

Watson Smith<sup>2</sup> has published a series of analytical data showing the variation in the composition of the tar derived from different qualities of coal when carbonised under constant conditions. Analyses of tars from American gasworks have been published by A. H. White and H. W. Hess.<sup>3</sup> The following data in regard to German tars obtained by distillation of coal in either horizontal or inclined retorts are due to Kraemer:<sup>4</sup>—

	Per cent.
Benzene and homologues . . . . .	2.50
Phenol and homologues . . . . .	2.00
Pyridine and Quinoline bases . . . . .	0.25
Naphthalene (and Acenaphthene) . . . . .	6.00
Heavy Oil, C <sub>n</sub> H <sub>n</sub> . . . . .	20.00
Anthracene and Phenanthrene . . . . .	2.00
Asphalt (Soluble Constituents of the Pitch) . . . . .	38.00
Carbon (Insoluble Constituents of the Pitch) . . . . .	24.00
Water . . . . .	4.00
Gases (loss on-distillation) . . . . .	1.25
	<u>100.00</u>

<sup>1</sup> Allen, *Commercial Organic Analysis*, 3rd ed., vol. ii., part ii., p. 54.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1889, 8, 950.

<sup>3</sup> *Ibid.*, 1900, 19, 509.

<sup>4</sup> *J. Gasbeleucht.*, 1891, 34, 225; *Wagner's Jahrbuch*, 1891, p. 47.

The average composition of the tar from four German gasworks, according to Kraemer and Spilker, are given in column I. of the following table; column II. gives the average composition of the tar from the Vienna gasworks, according to Rispler, during the years 1894 to 1897:—

	Sp. Gr.	I. Per cent.	II. Per cent.
Water . . . . .	—	3.77	4.77
Light Oil . . . . .	0.910 to 0.950	2.92	4.06
Middle Oil . . . . .	1.010	11.27	10.38
Heavy Oil . . . . .	1.040	9.00	6.11
Anthracene Oil . . . . .	1.100	15.60	13.71
Pitch . . . . .	—	55.40	60.49
Loss . . . . .	—	2.04	0.98
		<u>100.00</u>	<u>100.00</u>

Gas tars obtained by the older methods of working are distinguished by a high content of free carbon, which seldom amounts to less than 16 per cent., and often rises to 30 and even 35 per cent.<sup>1</sup> This considerably alters the consistency of the tars, and together with their usually higher percentage of naphthalene, distinguishes them from coke oven tars and from the gas tars obtained from vertical retorts. The latter have, according to W. Bueb,<sup>2</sup> the characteristics of a thin brown oil of sp. gr. 1.1000, and contain only from 2 to 4 per cent. of free carbon. Compared with ordinary gas tars, the percentage of naphthalene is about 50 per cent. less, while the percentage of pitch is much lower, and that of light hydrocarbons much higher. J. Bueb<sup>3</sup> gives the following data as the result of an experimental distillation of gas tar, from the same English coal, in Dessau vertical retorts and in horizontal retorts:—

	Vertical Retort. Per cent.	Horizontal Retort. Per cent.
Ammonia Water . . . . .	2.17	3.50
Light Oil . . . . .	5.85	3.10
Middle Oil . . . . .	12.32	7.68
Heavy Oil . . . . .	11.95	10.15
Anthracene Oil . . . . .	15.96	11.54
Pitch . . . . .	49.75	62.00

The following comparison between tars from vertical and inclined retorts is due to Schäfer:<sup>4</sup>—

	Vertical Retort. Per cent.	Inclined Retort. Per cent.
Water . . . . .	5.70	10.35
Light Oil up to 100° . . . . .	8.90	1.00
Light Oil 100° to 170° . . . . .	1.20	1.60
Middle Oil 170° to 230° . . . . .	13.50	7.50
Heavy Oil 230° to 270° . . . . .	7.30	10.70
Anthracene Oil above 270° . . . . .	29.30	18.80
Pitch . . . . .	34.10	58.13
	<u>100.00</u>	<u>100.00</u>

<sup>1</sup> Cf. Spilker, *Kokerei und Teerprodukte*, p. 38. <sup>2</sup> J. Gasbeleucht., 1905, 48, 835; 1906, 49, 955.

<sup>3</sup> Cf. Bertelsmann, *Entwicklung der Leuchtgaszerzeugung seit 1890*, p. 39.

<sup>4</sup> *Einrichtung und Betrieb eines Gaswerkes*, 1910, p. 194.



Compared with tar from ordinary retorts, dehydrated tar from T. Glover's chamber retorts<sup>1</sup> showed the following composition:—

	Chamber Retort. Per cent.	Ordinary Retort. Per cent.
Free Carbon . . . . .	11.10	23.20
Light Oil up to 170° . . . . .	0.40	1.40
Middle Oil to 270° . . . . .	10.20	10.50
Heavy Oil to 350° . . . . .	30.10	16.14
Pitch (soft) . . . . .	53.90	71.80
Naphthalene . . . . .	4.70	23.20

Gas tars from chamber retorts accordingly approximate in their composition to coke oven tars.

### (b) Coke Oven Tar.

Coke oven tar is usually more mobile than ordinary tar, since the content of free carbon does not exceed 10 to 12 per cent., and often amounts to only 2 to 6 per cent. It contains much less light and middle oils than gas tar, but more anthracene oil, and yields about the same quantity of pitch. Spilker gives the following data as representing the average composition of coke oven tar from Otto furnaces:—

	Per cent.
Specific Gravity . . . . .	1.145 to 1.191
Water . . . . .	2.69
Light Oil . . . . .	1.38
Middle Oil . . . . .	3.46
Heavy Oil . . . . .	9.93
Anthracene Oil . . . . .	24.76
Pitch . . . . .	56.44
Loss . . . . .	1.34
	<hr/> 100.00 <hr/>

While the tars produced in the various coke ovens in use on the Continent are in general similar in composition to the above, the tar resulting from the Jameson coke oven, which is worked in a few places in England, differs very materially. It contains no benzene, very little toluene, and rather more xylene. The greatest part of the distillate consists of oils belonging to the aliphatic series boiling between 250° and 350°; a small quantity of solid paraffin separates from the highest boiling fractions which correspond to the anthracene oils. Naphthalene and anthracene are not present, but there is a large proportion of acidic oils which contain no phenol and resemble wood tar creosote.<sup>2</sup>

<sup>1</sup> Cf. H. O'Connor, *J. Soc. Chem. Ind.*, 1910, 29, 471.

<sup>2</sup> Cf. Watson Smith, *Ibid.*, 1883, 2, 495.

## (c) Blast Furnace Tar.

This tar is only produced where the blast furnaces work with a suitable coal (principally in Scotland) and not with coke, as in Germany. It is quite different from the other coal tars, and contains considerably more acidic oils (including phenol and cresol, but chiefly, however, higher homologues), and a smaller proportion of aromatic hydrocarbons, but much paraffin. It contains a very high percentage of ash (flue ash), which reduces the value of the pitch. According to Watson Smith,<sup>1</sup> Scotch blast furnace tar has the following composition:—

	Per cent. by Volume.	Per cent. by Weight.	Sp. Gr.
Water . . . . .	30.60	32.3	1.007
Oil up to 230° . . . . .	2.91	2.8	0.899
Oil 230° to 300° . . . . .	6.97	7.1	0.971
Oil from 300° until the distillate solidified .	13.02	13.5	0.994
Soft Paraffin . . . . .	16.75	17.3	0.987
Coke . . . . .	...	21.5	...
Loss . . . . .	...	5.5	...

The water is strongly ammoniacal; the basic constituents of the tar oils (about 11 per cent. of the middle and heavy oils) correspond to those of ordinary coal tar.

The tar from gas producers closely resembles blast furnace tar.<sup>2</sup>

## (d) Water Gas Tar.

Water gas tar is invariably of an oily consistence, and usually of a brown colour, and is characterised by containing generally a very high percentage (up to 30 per cent.) of neutral water. This water is emulsified and very difficult to separate by ordinary means. It contains only traces of free carbon and of phenols. The higher boiling oils have a sp. gr. of over 1.00, and contain small quantities of naphthalene and anthracene.

Properly dehydrated water gas tar gives the following result when worked up on a large scale:—

Light and Middle Oil up to 230° . . . . .	About 20 per cent.
Heavy Oil to 300° . . . . .	30 "
Anthracene Oil above 300° . . . . .	15 "
Pitch . . . . .	30 "
Water and Loss . . . . .	5 "

Mathews and Goulden<sup>3</sup> determined the composition of a tar

<sup>1</sup> *J. Soc. Chem. Ind.*, 1883, 2, 495.

<sup>2</sup> *Cf. Lunge, Coal Tar and Ammonia*, vol. i., p. 128.

<sup>3</sup> *Wagner's Jahresber.*, 1892, p. 77.

obtained from water gas carburetted with crude Russian petroleum with the following result :—

	Per cent.
Benzene . . . . .	1.19
Toluene . . . . .	3.83
Light Paraffins . . . . .	8.51
Solvent Naphtha . . . . .	17.96
Phenols . . . . .	traces
Middle Oil . . . . .	29.44
Heavy Oil . . . . .	24.26
Naphthalene . . . . .	1.28
Crude Anthracene . . . . .	0.93
Coke . . . . .	9.80
	<u>97.20</u>

Such tar is unsuitable for working up into crude products for the aniline colour industry on account of the high percentage of paraffins.

#### (e) Oil Gas Tar.

As regards properties and composition, oil gas tar exhibits the greatest similarity to coal tar; it is distinguished, however, by a lower specific gravity, as well as by the almost entire absence of phenolic and basic substances, and of thiophene and homologues. It possesses the same deep black colour as coal tar, and has a similar odour, but is considerably less viscous owing to the low percentage of asphalt constituents. The content of free carbon varies within the limits of that in coal tar, but should not exceed from 20 to 22 per cent.

The following analysis of an oil gas tar, as prepared in the brown coal industry in Saxony and Thuringia, is given by Scheithauer :<sup>1</sup>—

	Per cent.
First Runnings from 70° to 110° and 150° . . . . .	5 to 10
Light Oil from 150° to 200° . . . . .	5 to 10
Middle Oil from 200° to 250° . . . . .	20
Heavy Oil from 250° to 300° . . . . .	20
Anthracene Oil over 300° . . . . .	30
Pitch and Loss . . . . .	10

Würth<sup>2</sup> found the following constituents in an oil gas tar of the same origin :—

	Per cent.		Per cent.
Benzene . . . . .	1.00	Naphthalene . . . . .	4.90
Toluene . . . . .	2.00	Crude Anthracene . . . . .	0.58
Xylene . . . . .	1.30	Phenols . . . . .	0.30
Resinifiable Oils below 150° . . . . .	1.00	Bases . . . . .	traces
Oils from 150° to 200° . . . . .	1.50	Asphalt . . . . .	22.00
Oils from 200° to 300° . . . . .	26.60	Free Carbon . . . . .	20.50
Oils from 300° to 360° . . . . .	12.60	Water (neutral) . . . . .	4.00

<sup>1</sup> *Fabrikation der Mineralöle*, p. 316.

<sup>2</sup> *Dissertation*, Munich, 1904.

Most of the characteristic constituents of coal tar, with the exception of carbon bisulphide and acridine, could be detected in this oil gas tar.

Letny<sup>1</sup> analysed an oil gas tar, prepared by passing heavy petroleum "tailings" through red-hot tubes with the object of converting them into aromatic hydrocarbons, with the following result:—

	Per cent.	
Water . . . . .	2.3	
Light Oil up to 90° . . . . .	4.6	Benzene, Toluene, Xylene, etc.
Light Oil from 90° to 140° . . . . .	5.2	
Middle Oil from 140° to 200° . . . . .	1.8	
Heavy Oil from 200° to 270° . . . . .	26.9	Naphthalene and unaltered Petroleum.
Anthracene Oil from 270° to 340° . . . . .	8.6	
Anthracene Oil above 340° . . . . .	27.5	Anthracene. Phenanthrene.
Pitch . . . . .	20.6	
Loss . . . . .	2.5	

The specific gravity of this tar, 1.207, was remarkably high.

### III.—THE EXAMINATION OF COAL TAR •

The value of coal tar as a raw material of chemical industry depends upon the quantity of aromatic hydrocarbons and phenols it contains, as well as upon the absence of members of the fatty series, olefines and paraffins. The analysis of crude tar includes the estimation of the specific gravity, of the uncombined carbon, and also a distillation test, which at the same time shows the quantity of ammonia water present.

#### (a) Sampling.<sup>2</sup>

This is effected by means of a syphon tube provided with a plug (Fig. 120). Samples should be taken from different parts of the vessel containing the tar, and should be well mixed before taking the final sample for examination.

#### (b) Estimation of the Specific Gravity.

Before estimating the specific gravity, a preliminary dehydration is necessary. This is carried out by putting the tar into a large covered beaker and keeping it in warm water, at a temperature not exceeding 50°, for twenty-four hours. The water separates and rises to the surface, and can be either decanted off or removed by means of filter paper. Köhler uses a tall bottle of thin glass having a narrow neck provided with a doubly perforated cork stopper (Fig. 121); a syphon fitted

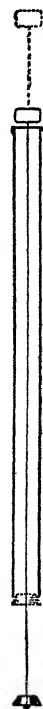


FIG. 120.

<sup>1</sup> *Dingl. polyt. J.*, 1878, 229, 253.

<sup>2</sup> *Cf. E. Senger, J. Gasbeleucht.*, 1902, 45, 841.

with a glass stopcock is fitted through one hole in the cork, and an air-tube, closed by a valve of rubber tubing, through the other. The bottle is frequently shaken by gently tapping it in order to accelerate the rise of the water to the surface. As soon as the water globules have disappeared from the sides of the lower part of the flask, the tar can be syphoned out, the first portion being rejected, as it always contains some water. The tar thus freed from water is allowed to cool to  $15^{\circ}$ .

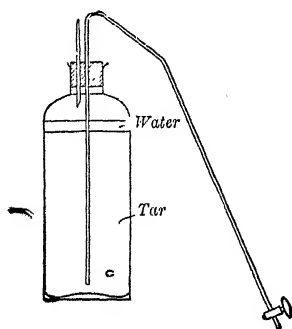


FIG. 121.

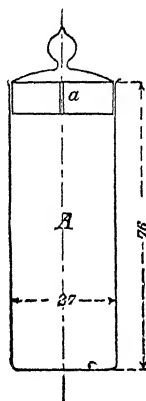


FIG. 122.

For the estimation of the specific gravity of the dehydrated tar, an ordinary pyknometer cannot be used on account of the viscosity of the tar at  $15^{\circ}$ . For this reason, Watson Smith<sup>1</sup> determines the weight of 1 litre, but this estimation is only of value when a good balance is used. Köhler uses a narrow-necked 100 c.c. flask, which is filled exactly to the mark from a dropping funnel. This enables the weighing to be made with great accuracy, but the filling of the flask by this method is slow, and in the case of very viscous tars is impossible. The use of a hydrometer for estimating the specific gravity of coal tars is not found to give results which can be depended upon, at all events not at a temperature of  $15^{\circ}$ . The apparatus devised by Lunge<sup>2</sup> (Fig. 122) gives absolutely exact results, and can easily be made from an ordinary weighing bottle. The glass stopper of the bottle A has a vertical groove, *a*, filed in it, which is about 2 mm. wide by 2 mm. deep. In estimating the specific gravity of tar by means of this apparatus, the same method is employed as in estimating that of solid substances. The tare (*a*) of the weighing bottle is first obtained, and then its weight (*b*) after it has been filled with water at  $15^{\circ}$ . It is then emptied and dried, and filled with tar to about two-thirds of its depth, after which it is placed, without its stopper, in hot water for one hour, until all the air-bubbles have been driven off. It is then allowed to cool, the total

<sup>1</sup> *J. Soc. Chem. Ind.*, 1883, 2, 496.

<sup>2</sup> *Z. angew. Chem.*, 1894, 7, 449.

weight ( $c$ ) of the flask plus tar taken, then filled up with water, the stopper replaced, and the last drops of water issuing through the groove removed. After allowing it to stand in water, the temperature of which is known, it is again weighed ( $d$ ). The specific gravity of the tar is then :—

$$\frac{c - a}{b + c - (a + d)}$$

### (c) Estimation of Free Carbon.

Kraemer's method<sup>1</sup> of estimating the quantity of free carbon in tar, is to warm a weighed quantity of the tar with forty times the amount of xylene in a water-bath until a homogeneous liquid is obtained. This is then filtered through a weighed filter paper, and the brownish black powder washed with xylene until the washings are colourless. This residue is then dried and weighed. According to Köhler, this dilute tar solution does not filter well, and a certain quantity of the finely divided carbon passes through the filter. The washed product also often contains traces of hydrocarbons of high molecular weight, which, as is well known, are very insoluble. He, therefore, recommends the following method:<sup>2</sup>—Ten grams of tar, together with a mixture of 25 g. of glacial acetic acid and 25 g. of toluene, are boiled in a conical flask under a reflux condenser, and the liquid passed through two filter papers folded together, which have previously been tared against each other. The residue is washed with hot toluene until the washings are colourless. In this way the carbon is obtained free from tarry impurities, and the amount of free carbon in the sample is found from the difference in weight of the two filters, after drying at 120° to constant weight.

Kraemer and Spilker<sup>3</sup> consider the following to be the most convenient method:—One part of the tar is warmed with three parts of aniline and the thin liquid poured on to an unglazed porous tile, which absorbs the soluble portions of the tar together with the aniline, and leaves the insoluble free carbon as a flaky mass. This is transferred without loss to a weighed watch-glass, with a wooden spatula, and weighed, after drying in a steam oven for several hours.

Important data with regard to the subsequent working up of the tar may be drawn from the amount of free carbon present. The yield of pitch can be calculated fairly accurately, assuming that the percentage of free carbon in pitch of the required hardness is known. If  $K$  is the percentage of carbon in the pitch and  $k$  the percentage in the tar, then,

$$K : 100 = k : x.$$

Good pitch of medium hardness, as now produced by most tar distillers, contains an average of 28 per cent. of free carbon. Thus, in

<sup>1</sup> *J. Gasbeleucht.*, 1887, 30, 849.

<sup>2</sup> *Dingl. polyt. J.*, 1888, 270, 233.

<sup>3</sup> Muspratt, *Handbuch der technischen Chemie*, 4th ed., 8, p. 3.

the case of a normal coal tar containing about 16 per cent. of free carbon, the quantity of pitch,  $x$ , is:—

$$x = \frac{100 \times 16}{28} = 57 \text{ per cent.}$$

Further, the behaviour of the tar on distillation can be foreseen with some certainty from the content of free carbon. Hodurek<sup>1</sup> estimates the free carbon as follows, and states that as ordinarily obtained it contains a large amount of bitumen:—One gram of pitch is treated with 200 c.c. of benzene, and the insoluble residue estimated after drying at 100°. In a second operation, 50 g. of pitch are dissolved in 150 g. of anthracene oil, filtered, 4 g. of the filtrate mixed with 200 c.c. of benzene, and the weight of the precipitate ("bitumen") so obtained estimated after drying at 100°. By subtracting this quantity of "bitumen" from the residue obtained in the first operation, the quantity of free carbon is obtained. This method is somewhat complex and lengthy, and does not give more reliable results than that of Kraemer and Spilker.

According to E. F. Hooper,<sup>2</sup> the free carbon content is directly proportional to the specific gravity, and may be calculated from the formula:—

$$\%C = 0.64 \times T - 10.0 \quad (T = \text{specific gravity of tar in degrees Twaddell}).$$

#### (d) Estimation of Water.

The crude tars are usually delivered to the tar distilleries in tank-wagons, more rarely in drums or in tank-barges. As a rule, part of the water, which is suspended in the tar in fine drops, separates on the surface during transit; in the case of light oil tars, it sinks to the bottom. The height of the water layer can be estimated by means of a glass syphon, and its quantity calculated. A water content of 4 or at most 5 per cent. is admitted in the case of gas and coke oven tars.

Two forms of apparatus are in use for the estimation of the percentage of water in the crude tar.

That of J. Becker,<sup>3</sup> which is used chiefly in gasworks, depends on the principle of vacuum distillation; it gives accurate results, and the estimation can be carried out in a short time.

The apparatus (Fig. 123) consists of a round-bottomed flask, *a*, of 4 to 5 litres capacity, fitted with a distillation-head, *b*, a Liebig's condenser, *c* (1 metre long), a worm-condenser, *d*, leading into the receiver *e*, a powerful water jet air-pump, *p*, attached to a manometer, *m*, and the mercury vessel *q*, and a Woulff's bottle, *n*, with three tubulures, placed between the manometer and the pump.

<sup>1</sup> *Öst. Chem. Zeit.*, 1904, p. 368.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1910, 29, 1437.

<sup>3</sup> *J. Gasbeleucht.*, 1902, 45, 764.

The apparatus shown on the left of the line *ii* is mounted at an angle of  $90^\circ$  to the apparatus shown on the right of the line, so that the manometer *m* is on the wall, the basin *o* in the middle of the bench, and the condenser, cooling worm, and receiver *e*, at the edge of the bench.

The estimation is carried out as follows:—About 1 kilo of the tar is poured into the flask, which is placed in a high sand-bath (lined with fine brick earth 0.5 cm. deep) and connected with the condenser as shown. The flask is heated until the tar begins to boil (the tap *k* being open and the clip *i* closed), which is indicated by numerous rapidly rising bubbles and by the condensation in the bulb *b*. The tap *k* is then closed and the water pump turned on; it is preferable to conduct the distillation in a vacuum of 400 mm., and towards the end of the distillation at 700 mm.—*i.e.*, when the mercury column of the manometer has risen to 40 or 70 cm. respectively.

The tar soon begins to froth up and rises into the neck of the flask; it is driven back by admitting air into the flask by a momentary pressure of the clip *i*. This operation is repeated until nearly all the water has been expelled, which is recognised by the cessation of the crackling noise in the flask. The distillation is continued until, at the highest vacuum, only oils condense on the sides of the flask and wash it clear from the tar froth. As soon as this point is reached, the flame

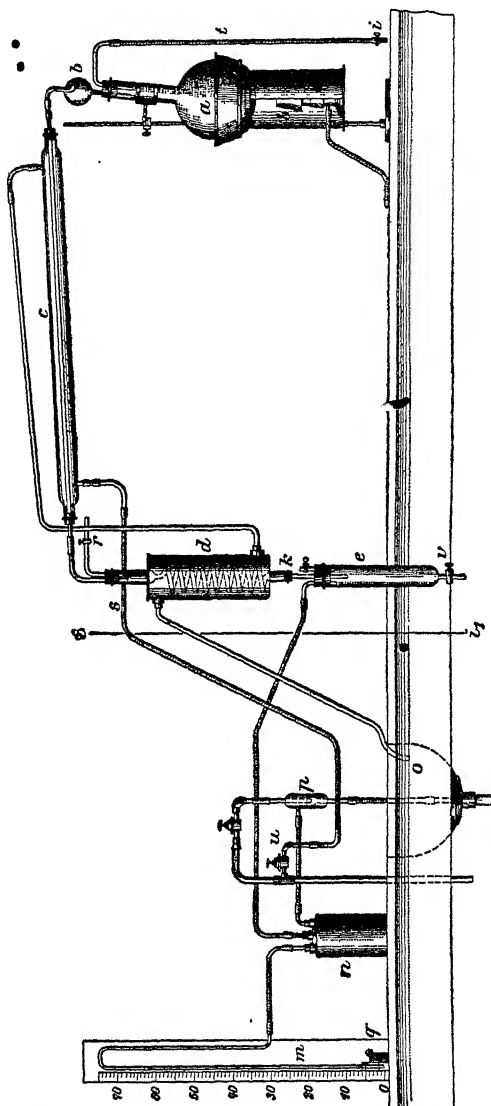


FIG. 123.



is turned out, the clip *i* opened, and, after a few minutes, the pump stopped. The distillate in the receiver *e* separates into two layers, the oil above and the water below; the latter is drawn off through the tap *v* into a tared beaker and weighed.

If any tar should get into the condenser, air is subsequently admitted through *v* or *k* and not through *i*, and the tar and oils thus driven back into the flask. Becker states that ten determinations can be carried out by this method in one day.

The second form of apparatus is considerably simpler than the foregoing, and requires less attention; it is the method usually adopted in the tar distilleries, and is based on the large scale method of distillation. No frothing over of the tar need be feared, and the estimation is easily finished in three-quarters of an hour. E. Senger<sup>1</sup> describes the method as follows:—

A sample of 0.5 kilo, previously well mixed in a large mortar, is distilled from a copper still (Fig. 124) of about 1 litre capacity, 12 cm. in height, and 13 cm. diameter; for purposes of cleaning, the lid is

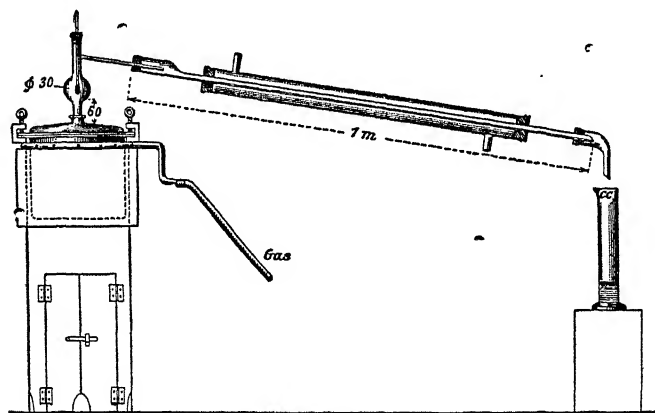


FIG. 124.

detachable, and is fastened with four or six clamps. A cardboard or asbestos ring, preferably coated with a cement of linseed oil and powdered chalk, is placed as a packing between the still and its lid. The still is suspended in a sheet-iron furnace, the upper part of which is jacketed, while below it is provided with a small door and with air openings.

The water is first of all completely driven off by heating with gas, which is delivered through a gas pipe perforated on the inside and placed round the upper part of the still; heating from below is unnecessary during this operation, but if middle oil, heavy oil, etc., are to be estimated, a Bunsen burner is placed in position through the

<sup>1</sup> *J. Gasbeleucht.*, 1902, 45, 841.

small door, and the still subsequently heated only from below. In the estimation of water, the distillation is continued until the oil passing over is free from drops of water, which occurs at about 200°. A measuring cylinder serves as a receiver, and the volume of water collected is read off. Should the graduations be obscured by the separation of crystals, the water is filtered into a second cylinder through a small, moistened filter paper.

Kraemer and Spilker<sup>1</sup> employ a metal still holding about 2 litres, and distil as long as an aqueous distillate passes over. Tars which froth much (containing much carbon) are mixed with half their weight of water-free, heavy tar oil, whereby frothing over is avoided with certainty. Maiwald<sup>2</sup> recommends the addition of 40 to 50 per cent. benzol to avoid frothing over.

H. Beck<sup>3</sup> has recently described a method in which the crude tar (200 g.) is allowed to drop into water-free tar or tar oil (500 g.) heated to 250° to 270°, which is contained in an iron retort of 2 litres capacity provided with a dropping funnel and a Liebig's condenser. If the addition is properly carried out, no frothing occurs, and each drop gives up its water with almost explosive violence; a measuring cylinder is employed as the receiver. It is stated that the estimation can be carried out in thirty-five minutes, even when the tars contain 50 per cent. of water.

The percentage of water in tar generally increases with the content of free carbon.

#### (e) Distillation Test.

A distillation test performed in a glass retort, such as that described by Lunge and R. Schmid,<sup>4</sup> cannot be relied on, on account of the difficulty of exactly reproducing the manufacturing conditions, and is consequently never employed.

In tar distilleries an apparatus similar to that of Senger for the estimation of the water in tar is employed (p. 762).

According to Kraemer and Spilker, it is sufficient, as a rule, to estimate the quantity of water; this analysis at the same time gives the content of light benzol. If a complete distillation test be required, this is carried out with 5 kilos of tar in a cast-iron retort having a capacity of 8 litres, if possible under reduced pressure, and the successive fractions are collected, similarly to the procedure on a large scale.

• If the distillation is carried out at the ordinary pressure, the distillate is collected in the following fractions:—

1. Light oil up to 170°.

<sup>1</sup> *Chem. Ind.*, 1887, 10, 337.

<sup>2</sup> *Chem. Zeitschr.*, 11., p. 533.

<sup>3</sup> *Chem. Zeit.*, 1909, 33, 591.

<sup>4</sup> *Chem Ind.*, 1887, 10, 337.

2. Middle oil up to 200°.
3. Creosote oil up to 270°.
4. Anthracene oil up to the end of the distillation, which should be continued until the desired melting point (about 60° to 65°) of the residual pitch is reached.

The further examination of the *Light Oil* will be dealt with later.

The *Middle Oil* is allowed to stand for several days, in order to separate the naphthalene, and, if necessary, artificially cooled.

The *Creosote Oil* is treated in the same way; the naphthalene obtained from both these fractions by filtering and pressing is united and considered as "crude naphthalene."

The *Anthracene Oil* is left for three to four days after cooling, as the anthracene only crystallises out slowly. The crude anthracene is filtered off on linen, pressed when cold, and sometimes warmed on porous tiles to 30° to 40° and again pressed before weighing. The contained anthracene is then estimated as described below (p. 804).

This first distillation of coal tar gives the following data as to its value:—

1. Content of Light oil.
2. Content of Middle oil.
3. Content of Creosote oil.
4. Content of Raw naphthalene.
5. Content of Anthracene (green) oil.
6. Content of Raw anthracene.
7. Content of Pitch.

The quantities of the two first fractions are too small to render a detailed analysis of them possible. Their examination must be confined to a distillation test and to the estimation of the phenols and of the non-nitratable hydrocarbons; for the rest, comparative tests must be made during the practical working.

## B. INTERMEDIATE PRODUCTS

The working up of coal tar consists in an initial distillation, over an open fire, in wrought-iron stills which have a capacity of up to 50 tons, whereby the above four fractions are separated, the successive separations being controlled either by the temperature of distillation or by the specific gravity of the distillate; a partial vacuum may be used to aid the distillation, and, in some cases, a continuous distillation process is employed.

The four fractions thus obtained are subjected to further distillations, partly over open fires and partly by steam, in stills, either with or without dephlegmating columns, the phenols removed by treatment with alkali, the bases by treatment with dilute acid, the solid con-

stituents (naphthalene and anthracene) separated by filtration and pressing, and the hydrocarbons finally purified by treatment with concentrated sulphuric acid.

A full description of the methods employed is given in Prof. Lunge's work on "Coal Tar and Ammonia."

The properties, composition, methods of examination, and products obtained from each of these four fractions are described in the sequel, together with the most important methods of control in working.

#### I.—LIGHT OIL (FIRST RUNNINGS, CRUDE NAPHTHA)

**Properties.**—A yellow to dark brown mobile liquid of sp. gr. 0.910 to 0.950 with a penetrating smell reminiscent simultaneously of ammonium sulphide, carbolic acid, and naphthalene. A green fluorescence of some specimens is due to tar mechanically carried over. It begins to boil at 80° to 90°; 30 to 50 per cent. distils over up to 120° (the limit for benzol for aniline), 50 to 80 per cent. up to 160° (the limit for the xylenes), and 90 per cent. between 170° and 220°. According to Spilker, the light oil from coke oven tar often contains much higher boiling fractions, and for such light oils the above percentages approach the upper limits; were this found to be the case in gas tar, it would indicate a badly conducted distillation or an abnormally high percentage of water in the tar from which the light oils were obtained.

Rispler<sup>1</sup> has published the following distillation analyses or yields, which indicate the difference between the light oil from gas and coke oven tar respectively:—

Distillate.	Light Oil from Gas Tar.	Light Oil from Coke Oven Tar.
Up to 100° . . .	10 per cent.	6 per cent.
Up to 135° . . .	47 "	29 "
Up to 165° . . .	69 "	42 "
Up to 195° . . .	85 "	58 "
	Light Oil from Vienna Gas Tar.	Light Oil from Rhenish Westphalian Coke Oven Tar.
Up to 135° (Crude Benzol I.) .	36.12 per cent.	12.66 per cent.
Up to 165° (Crude Benzol II.) .	15.69 "	16.42 "
Up to 200° (Carbolic Oil) .	18.01 "	18.47 "
Residue (Heavy Oil) .	26.51 "	46.36 "
Water and Loss .	3.67 "	3.09 "
	<u>100.00</u>	<u>100.00</u>

**Composition.**—According to Kraemer and Spilker, light oil contains the following classes of substances in the approximate proportions given:—

*Phenols* (technically termed "Acid Oils"), 5 to 15 per cent.

<sup>1</sup> *Chem. Zeit.*, 1910, 34, 545.

*Bases* (Pyridines), 1 to 3 per cent.

*Sulphur Compounds* (Carbon bisulphide, Thiophene and its homologues), about 0.1 per cent.

*Nitriles*, 0.2 to 0.3 per cent.

*Neutral Substances* containing oxygen (Acetone, Cumarone), 1.0 to 1.5 per cent.

*Hydrocarbons*, 80 to 100 per cent.

The last consists chiefly of aromatic hydrocarbons of which four-fifths is benzene and its homologues, and one-fifth naphthalene. The remaining hydrocarbons are Olefines, 3 to 5 per cent.; Paraffins, 0.5 to 1.0 per cent.; and Cyclic Hydrocarbons, both saturated and unsaturated (the latter of which absorb bromine), 1.0 to 1.5 per cent.

The percentages of the individual benzene hydrocarbons in the mixture diminish as their boiling points rise (Kraemer and Spilker); the ratio of benzene, toluene, the xylenes, and tri- and tetra-methylbenzenes is approximately 100, 30, 15, 10, and 1.

### The Examination of Light Oil.

The works' tests are confined to the determination of the specific gravity and of the boiling point of the crude oil, the specific gravities of the crude benzol fractions coming over at temperatures up to 120° and up to 160°, and the estimation of the phenols, bases, and naphthalene.

*Specific Gravity.*—This is usually determined with the hydrometer, or Mohr's balance; it varies with the boiling point, and in the case of normal light oils, of which 90 per cent. boils below 200°, its value is about 0.930. Values of above 0.950, and below 0.900 with the above boiling point, indicate an abnormal composition or admixture with other oils, such, for instance, as the distillates of oil gas tar or the distillates from the lignite and petroleum industries.

*Boiling point.*—For the determination of the boiling point—*i.e.*, the range of temperature within which each fraction distils over—glass retorts are still largely used in England. In Germany, retorts of copper, rarely of glass, are in fairly general use, and have a capacity of about 150 c.c. They are provided with a thermometer, and connected to a Liebig's condenser. One hundred c.c. of the oil to be tested are taken, and the fractions obtained through every 10° rise of temperature are received in graduated cylinders mounted on a rotating stand, so as to ensure the uninterrupted collection of the several fractions. The distillation is continued until at least 95 per cent. has distilled, so that the distillate can be used at once for further examina-

tion. The fractions up to  $120^{\circ}$  are united, and tested for specific gravity, which in the case of good light oil should be from 0.880 to 0.885. A lower specific gravity shows the presence of paraffins. From the fractions above  $180^{\circ}$  the naphthalene will separate out at the ordinary temperature, and can be estimated after it has been pressed between filter papers or drained on a porous tile.

*Acid Oils (Phenols) and Bases (Pyridines).*—For these estimations all the fractions are united (the graduated measures being washed with xylene) and shaken up in a graduated cylinder together with 100 c.c. of sodium hydroxide (sp. gr. 1.100). The volume of the alkaline solution is read off after the liquids have separated. Each increase of 1 c.c. in volume represents 1 per cent. of acid oils. For a more exact estimation, the sodium hydroxide solution is carefully separated from the oil, evaporated on the water-bath until no further cloudiness results on the addition of water, then cooled, acidified with hydrochloric acid, and salted out with common salt. The volume of the phenols, which separate out, is measured, and calculated as 1 per cent. for each cubic centimetre.

The quantity of the bases is found by shaking up the oil, previously washed with sodium hydroxide solution, with 30 c.c. of 20 per cent. sulphuric acid. After allowing to settle, the increase in volume of the sulphuric acid is noted. A control determination can be effected by evaporation of the acid solution and precipitation of the bases by a large excess of sodium hydroxide (sp. gr. 1.4).

To determine the quantity of pyridine and its homologues that are present in the total bases, the mixture of bases and excess of sodium hydroxide, as obtained in the preceding estimation, is submitted to distillation until the distillate no longer tastes of pyridine. The distillate, amounting to about 50 c.c., is diluted to 200 c.c. with absolute alcohol, and 10 c.c. of the mixture treated with 50 c.c. of absolute alcohol and about 2 c.c. of a saturated, aqueous solution of cadmium chloride. After standing for twenty-four hours, the white crystals of the double salt of the bases and cadmium chloride which have separated out, are collected upon a tared filter, dried at  $100^{\circ}$ , and weighed. One hundred parts of the double salt represent forty-six parts of pyridine bases.

In English works, the examination of the first runnings and of the light oils for their yield of valuable constituents (benzene, toluene, xylene, solvent naphtha, and phenol), is carried out by the method of G. E. Davis,<sup>1</sup> which agrees in its essentials with that previously proposed by Lunge.<sup>2</sup> Two hundred c.c. of the oil ("crude naphtha")

<sup>1</sup> *J. Soc. Chem. Ind.*, 1885, 4, 645.

<sup>2</sup> *Coal Tar and Ammonia*, pp. 747 et seq.

are well shaken for five minutes with 20 c.c. of sulphuric acid of sp. gr. 1.84 in a pear-shaped separating funnel of 300 c.c. capacity. The tarry sulphuric acid is carefully drawn off from the dark oil above, the latter washed twice with 300 c.c. of water, in the funnel, then with 30 c.c. of sodium hydroxide solution of sp. gr. 1.060, once more with 30 c.c. of water, and the volume of the residual oil measured. The difference between this and the original quantity represents the "loss on washing." The oil is then distilled from a round-bottomed 200 c.c. flask with a Le Bel-Henninger or Hempel column, as many cubic centimetres of the washed oil being taken as correspond to the percentage obtained on washing. A Liebig condenser is attached and the flask heated in a sand- or air-bath so that one drop passes over every two seconds. The distillate up to 120° is collected in a graduated cylinder, and the receiver changed to collect the portion passing over up to 170°. The burner is removed before each change of the receiver, and the condenser allowed to completely empty itself. The distillate up to 120° consists principally of a mixture of benzene and toluene; that from 120° to 170° is taken as solvent naphtha, and gives by fractionating 90 per cent., boiling between 125° and 160°. The residue remaining in the flask, which generally solidifies on cooling, is considered as creosote oil.

For the approximate estimation of the products contained in the first fraction, Davis gives the following tables:—

A. Mixtures of 90 per cent. and 50 per cent. Benzol.

Benzol.		First Drop.	Percentage distilled at 100°.	Percentage distilled at 120°.
90 per cent.	50 per cent.			
0	100	92°	50	90
5	95	92°	51	92
10	90	91°	51.5	92
15	85	91°	53	92
20	80	90°	55	92
25	75	90°	60	93
30	70	90°	65	93
35	65	90°	67	94
40	60	88°	69	94
45	55	88°	70	94
50	50	87°	71	94
55	45	87°	73	94
60	40	86°	76	95
65	35	86°	78	95
70	30	86°	79	96
75	25	85°	84	96
80	20	85°	84	97
85	15	84°	86	97
90	10	84°	88	Dry
95	5	84°	89	"
100	0	84°	90	"

## B. Mixtures of 50 per cent. Benzol and Commercial Toluene.

Mixture of		First Drop.	Percentage distilled at 100°.	Percentage distilled at 105°.	Percentage distilled at 110°.	Percentage distilled at 120°.
50 per cent. Benzol.	Toluene.					
100	0	92°	50	68	80	91
95	5	93°	45	64	76	91
90	10	94°	33	60	73	90
85	15	94°	30	58	73	90
80	20	95°	28	57	72	90
75	25	95°	26	55	71	90
70	30	96°	22	48	67	90
65	35	96°	19	47	65	90
60	40	96°	15	46	65	90
55	45	97°	12	44	65	90
50	50	98°	8	42	64	90
45	55	98°	4	34	57	90
40	60	99°	0	26	56	90
35	65	100°	0	25	55	90
30	70	100°	0	23	53	90
25	75	100°	0	21	53	90
20	80	100°	0	16	48	90
15	85	101°	0	14	46	90
10	90	102°	0	13	45	90
5	95	103°	0	10	44	90
0	100	103°	0	0	39	90

## C. Mixtures of 90 per cent. Benzol and Commercial Toluene.

Mixture of		First Drop.	Percentage distilled at 100°.	Percentage distilled at 105°.	Percentage distilled at 110°.	Percentage distilled at 120°.
90 per cent. Benzol.	Toluene.					
0	100	103°	0	7	50	94
5	95	102°	0	21	59	94
10	90	101°	0	30	66	94
15	85	100°	0	38	68	95
20	80	97°	9	43	73	95
25	75	95°	16	53	76	95
30	70	95°	23	59	78	96
35	65	94°	33	60	80	96
40	60	93°	43	66	82	96
45	55	92°	46	71	85	97
50	50	91°	52	72	86	97
55	45	91°	58	76	86	97
60	40	91°	60	78	88	97
65	35	90°	65	81	89	97
70	30	89°	71	83	91	97
75	25	88°	75	85	91	98
80	20	87°	77	87	92	98
85	15	86°	83	89	93	98
90	10	85°	85	91	94	Dry
95	5	84°	88	93	95	"
100	0	84°	90	94	96	"



*Example.*—A sample of crude naphtha gave the following results by Davis's method :—

Loss on washing, 18.5 per cent.

Distillate up to 120° (benzene), 45 per cent.

Rectification of above,  $\frac{100^\circ}{71} \cdot \frac{120^\circ}{94}$ , *i.e.*, 50 per cent. of 90 per cent. benzol and 50 per cent. of 50 per cent. benzol, according to Table A.

Distillate up to 170°, 10 per cent.

Rectification of same,  $\frac{126^\circ}{0} \cdot \frac{160^\circ}{92}$ .

The actual working results obtained in practice were :—

90 per cent. benzol, 23 per cent. }  
 50       "       "       24       "       } 47 per cent.  
*(i.e., each about 50 per cent.).*

Solvent naphtha, 10.4 per cent.

Rectification of same,  $\frac{130^\circ}{1} \cdot \frac{160^\circ}{94}$ .

Loss on washing, 20 per cent.

### The Working up of Light Oil.

The oil is redistilled, and yields the following intermediate products according to the hydrometer readings :—

(a) Light benzol up to 0.89 sp. gr.

(b) Heavy benzol up to 0.95 sp. gr.

(c) Carbolic oil up to 1.00 sp. gr.

The distillations are stopped when a considerable separation of naphthalene commences. The residue is united with the crude middle oil, and the carbolic oil mixed with the corresponding fraction from middle oil, and both further worked up as subsequently described.

The further working up of the crude benzols is carried out in the benzene works, where repeated washings with caustic soda and with strong sulphuric acid are followed by rectification with a dephlegmating column. Similar fractions are then united and the final products form the usual grades of commercial benzene.

The control of the working conditions extends chiefly to testing the purity of the washed benzols—*i.e.*, their behaviour to concentrated sulphuric acid and to bromine, as will be described later. For this purpose samples of 100 c.c. are removed from the sulphuric acid washing process, and shaken in a separating funnel, first repeatedly with water, then with sodium hydroxide solution of sp. gr. 1.1, and finally with 50 c.c. of distilled water. Sixty c.c. of each sample are then distilled in the above-mentioned small copper still and the

distillate tested with bromine and with concentrated sulphuric acid. According to the result of these tests, the washing process, consisting of the removal of the acid resin and further treatment with 1 per cent. quantities of sulphuric acid, is repeated until the washed product corresponds to the standard of purity required. The yield of final products is determined by careful distillation with a fractionating column (cf. *infra*).

## II.—MIDDLE OIL

**Properties.**—When completely liquid—*i.e.*, at 40°, as it comes from the condensers, it forms a yellow or brownish oil possessing a slightly sharp but distinct odour of carbolic acid and naphthalene; the specific gravity (measured at 40° and calculated to 15°) is not below 1.00, and on the average amounts to about 1.02. At the ordinary temperature it is solid or semi-solid owing to the contained naphthalene. The oil, which can be separated by draining or straining the mass, should usually distil up to 250° and have a sp. gr. of 0.99 to 1.01. Kraemer and Spilker give the following results of the distillation of crude and of drained-off middle oil:—

Temperature.	Crude Oil.	Drained-off Oil.
°C.	Per cent.	Per cent.
160—170	5	4
180	10	10
190	20	25
200	35	43
210	55	58
220	70	75
230	80	81
240	85	86
250	88	88
255	90	90

The boiling points of middle oil vary according to its origin.

Rispler<sup>1</sup> obtained the following results by working up the middle oils from gas tar and from coke oven tar:—

Distillates.	Middle Oil from Gas Tar.	Middle Oil from Coke Oven Tar.
Up to 165° (Crude Benzol II.)	4.15 per cent.	1.78 per cent.
Up to 195° (Carbolic Oil)	21.77 "	19.91 "
Up to 220° (Naphthalene).	43.45 "	28.68 "
Residue (Heavy Oil)	26.91 "	48.18 "
Water and Loss	3.72 "	1.45 "

**Composition.**—The chief constituent is naphthalene, which may amount to 40 per cent. The most important of the liquid constituents

<sup>1</sup> *Chem. Zeit.*, 1910, 34, 545.

are the phenols, 25 to 35 per cent., of which about one-third consists of ordinary phenol, and two-thirds of its homologues, principally the isomeric cresols with a small quantity of xylenol. According to Rispler,<sup>1</sup> the middle oil from gas tar contains up to 50 per cent. of naphthalene and about 25 per cent. of acid oils; that from coke oven tar, on the other hand, contains only up to 43 per cent. of naphthalene, and not more than 13 per cent. of acid oils. The two methylnaphthalenes also occur in middle oil, which further contains, on an average, about 5 per cent. of basic substances, comprising considerable quantities of pyridines, quinoline, and quinaldine, boiling from 239° to 242°. Spilker's explanation of the remarkable fact that pyridine, which boils at 115°, is met with in considerable quantity in the relatively high boiling middle oil, is that it combines with the phenols to form compounds which only begin to distil at 180° to 190°. These compounds are only decomposed on treatment with sodium hydroxide solution, a fact which is to be borne in mind in working up the oils, since the extraction of bases can only take place after the removal of phenols by treatment with caustic soda.

#### The Examination of Middle Oil. •

This comprises the determination of the boiling point and specific gravity of the crude oil, the percentage of naphthalene, the boiling point and specific gravity of the oil after crystallisation of the naphthalene, the boiling point of the naphthalene, and the percentage of phenols and of bases in the oil freed from naphthalene. The latter determinations are carried out as described under Light Oil.

*Naphthalene.*—To determine the naphthalene, from 0.5 to 2 kg. of the previously liquefied oil are allowed to stand for twenty-four hours with frequent stirring. The crystals which separate are filtered on the pump, pressed between linen or filter paper in a hand-press till no longer oily to the touch, and weighed.

To determine the boiling point of the crude naphthalene, 100 g. of the pressed material are distilled from a copper retort, the distillate collected in separate porcelain dishes for every degree rise of temperature, and weighed.

*Phenols and Bases* are estimated as described under Light Oil, p. 767. The examination of the phenols is carried out as described under Carbolic Oil, p. 773.

A good Middle Oil should have the following properties:—The specific gravity should be at least 1.0 at 15°. At least 90 per cent. should boil below 260°, and it should contain at least 30 per cent. of naphthalene, boiling between 210° and 220°. The boiling point of the oil when freed from naphthalene should average 250°; its specific

<sup>1</sup> *Chem. Zeit.*, 1910, 34, 545.

gravity should then be from 0.99 to 1.01, and it should contain 5 per cent. of bases and 25 to 35 per cent. of phenols. The boiling point of the phenols should start at 180°, after driving off the water, and rise to about 210°; at 190° at least 25 per cent. of the phenols should have distilled over.

**The Working up of Middle Oil.**—By distillation in direct fired stills middle oil yields the following fractions according to the hydrometer readings:—

- (a) Carbolic Oil up to 1.00 sp. gr., about 20 per cent.
- (b) Naphthalene Oil not exceeding 1.025 sp. gr., about 30 per cent.
- (c) Residue, = Heavy Oil, about 50 per cent.

Fraction (a) is equivalent to fraction (c) from Light Oil, and is added to it; fraction (b) corresponds essentially to fraction (a) from Creosote Oil (p. 775), and is worked up with it. The residue (c) is transferred to the Heavy Oil. According to the purity of the crude Middle Oil, it is distilled either at once or after previous separation of naphthalene by refrigeration.

### III.—CARBOLIC OIL

**Properties.**—Carbolic Oil has a similar smell to Middle Oil, and a sp. gr. of 1.00 to 1.005. At the ordinary temperature it is thick, owing to the contained naphthalene. It boils between 160° and 250°.

**Composition.**—It contains from 25 to 40 per cent. of phenols, an equal proportion of naphthalene, and about 7 per cent. of bases; about one-third of the naphthalene remains in solution after the oil has cooled. The phenols contain a greater proportion of benzene phenol than of cresols.

#### The Examination of Carbolic Oil.

Carbolic Oil is examined in the same manner as Light Oil and Middle Oil.

**Phenols.**—For the estimation of the phenols, at least 500 c.c. of the carbolic oil is extracted with sodium hydroxide solution of sp. gr. 1.1, and steam blown through the alkaline solution, on a sand-bath, until the distillate is clear and almost odourless. The phenols are then precipitated by the addition of hydrochloric acid and a saturated solution of common salt, and washed once with water, which must be carefully removed.

In valuing the crude phenol obtained, or any sample of crude commercial phenol, the quantity of water, the setting point, and the solubility should be determined. All three determinations are performed

in one operation, according to Lowe's method,<sup>1</sup> which is generally carried out as follows:—

A 150 c.c. distilling flask is employed, the delivery tube of which is connected by a cork with a condensing tube 50 cm. long and of 10 mm. bore; the flask is fitted with a thermometer, so that the progress of the distillation may be observed. One hundred c.c. of the crude phenol are taken, the water driven off by heating and collected in a 25 c.c. graduated cylinder; the water is considered to be completely expelled when 10 c.c. of oil (phenol) are present below it in the cylinder. Experience has shown that these 10 c.c. may be considered to consist of equal parts of phenol and water. If the oil floats on the water it is Light Oil, and indicates incomplete separation from the sodium phenate solution during the washing of the Light Oil. The separation of the water can be very quickly effected without loss by using as the receiver a 2-litre flask, into the body of which the end of the condenser is inserted, until the temperature rises to 150°. It is very important that all moisture should be completely expelled by heating the whole length of the condenser, especially on its upper side and at the point where it is connected to the distilling flask. The neck of the distilling flask must also be freed from water by heating it with a flame in the same way. These precautions are absolutely necessary, as even traces of water would lower the setting point of the carbolic acid which distils over next. At 150°, the distillation is interrupted and the contents of the receiver emptied into a 25 c.c. cylinder, in which the oil will measure 7 to 8 c.c. The distillation is then continued until the total oil in the distillate measures exactly 10 c.c. The receiver is now changed for a 100 c.c. graduated cylinder and the distillation continued so slowly that the distillate is cold before reaching the cylinder; 62.5 c.c. are distilled off in this way. The residue in the retort is valueless for the manufacture of carbolic acid and cresol.

The 62.5 c.c. of distillate thus obtained are used for the determination of the setting point, as follows:—A thermometer, reading to tenths of a degree from 10° to 40°, and the scale of which commences about 15 cm. above the bulb, is used for the determination. The cylinder is first cooled in ice and water to below the probable setting point. A small crystal of phenol is then stirred into the liquid with the thermometer to hasten the crystallisation. During solidification the temperature rises, and the highest point reached, at which the mercury remains stationary for at least one minute, is taken as the setting point. For good, crude phenols this should lie between 15.5° and 24°.

For comparison, standard mixtures of pure crystallised carbolic acid and cresol (preferably tar cresol, a mixture of the three isomers) are used, the setting points of which have previously been determined.

<sup>1</sup> Lunge, *Coal Tar and Ammonia*, p. 608.

Mixtures of phenol with pure ortho-, meta-, or para-cresol, the melting points of which were investigated by Lunge and Zschokke,<sup>1</sup> cannot be used, as Lunge<sup>2</sup> has pointed out, since coal tar cresol contains all three isomers, and the proportions of the isomers in cresols from various sources are not identical.

*Crude Naphthalene* is determined as described under Middle Oil (p. 772), and *Bases* as described under Light Oil (p. 767).

**The Working up of Carbolic Oil.**—After the separation of the contained naphthalene by filtration and pressing, the residual oil is usually subjected to a further distillation whereby the chief fraction obtained boils between 160° and 205° and contains about 30 per cent. of phenols. The subsequent treatment comprises:—

- (a) Dissolving the acidic constituents in caustic soda.
- (b) Removal of the bases with dilute sulphuric acid.
- (c) Steaming and subsequently precipitating the phenols and bases respectively.
- (d) Purification of the products obtained in (c), either by fractional distillation or by recrystallisation.

#### IV.—CREOSOTE OIL OR HEAVY OIL

**Properties.**—Creosote Oil is a semi-liquid product, having a smell resembling that of naphthalene and carbolic acid; it distils between 200° and 300°, and has an average sp. gr. (including about 20 per cent. of solid constituents) of 1.04.

**Composition.**—The solid constituents comprise naphthalene, acenaphthene, and allied hydrocarbons; the liquid constituents consist of from 8 to 10 per cent. of phenols (chiefly cresols and higher homologues), about 6 per cent. of pyridine bases, and about 70 per cent. of hydrocarbons of unknown constitution which await further investigation. Rispler<sup>3</sup> found about 28 per cent. of naphthalene and 16 per cent. of acidic compounds in gas tar, and about 32 per cent. of naphthalene and 10 per cent. of acidic compounds in coke oven tar.

**Method of Examination.**—This includes the determination of the sp. gr. and the estimation of the solid constituents (naphthalene), the acidic compounds, and bases, according to the methods described above. The oil is also distilled and the following fractions separated:—

(a) Naphthalene Oil I., which is the equivalent of fraction (b) of Middle Oil, and which is purified and worked up with it.

(b) Naphthalene Oil II. This fraction is collected until no more naphthalene separates out in the distillate.

(c) Residue = Anthracene Oil.

<sup>1</sup> *Chem. Ind.*, 1885, 8, 6.

<sup>2</sup> *Coal Tar and Ammonia*, p. 617.

<sup>3</sup> *Chem. Zeit.*, 1910, 34, 545.

For further details as to the examination of creosote oils see under "Final Products," p. 829.

#### V.—NAPHTHALENE OIL

**Properties and Composition.**—Naphthalene Oil I. boils between  $180^{\circ}$  and  $230^{\circ}$ , and separates about 40 per cent. of almost pure naphthalene on standing; it contains about 15 per cent. of acid oils and a small proportion (up to 3 per cent.) of basic constituents.

Naphthalene Oil II. boils between  $200^{\circ}$  and  $280^{\circ}$ , and also contains a considerable quantity of crude naphthalene, but which is mixed with acenaphthene and methylnaphthalene, which necessitates a further distillation. The other constituents are acid oils (homologues of cresol), hydro-naphthalenes, diphenyl, quinoline bases, etc.

**The Working up of Naphthalene Oil.**—The liquid portion of Naphthalene Oil I., after separation of the solid naphthalene, is termed "crude carbolic acid." It contains from 25 to 30 per cent. of phenols, and is worked up by fractional distillation to products containing up to 50 per cent. of phenols. The oil from Naphthalene Oil II. is a creosote oil, which is used in admixture with anthracene oil for preserving railway sleepers, telegraph poles, and the like.

The crude naphthalene is pressed, then washed successively with concentrated sulphuric acid, caustic soda, and water, and either distilled or sublimed.

The **Methods of Examination** have been described above.

#### VI.—ANTHRACENE OIL.

**Properties.**—This last fraction in the distillation of tar has a sp. gr. of 1.1 and boils between  $280^{\circ}$  and  $400^{\circ}$ ; it has a greenish yellow colour, which darkens gradually to greenish brown, and possesses a characteristic smell different from that of the other tar oils. Anthracene oil is liquid at  $60^{\circ}$ , but on cooling to the ordinary temperature separates from 6 to 10 per cent. of crude anthracene as a greenish yellow powder containing from 25 to 30 per cent. of pure anthracene. In contrast to the other tar oils, it possesses a certain viscosity which renders it applicable as a lubricant for rough purposes.

**Composition.**—Anthracene oil contains from 2.5 to 3.5 per cent. of pure anthracene; the other solid constituents include phenanthrene, carbazol, fluorene, acridine, etc. The proportion of phenols, for the most part of unknown constitution, is about 6 per cent. Comparatively little is known of the nature of the remaining liquid constituents.

**Methods of Examination.**—These comprise the determination of the specific gravity, and of the boiling point and the estimation of the contained anthracene, which is effected by the method described below (p. 804).

**The Working up of Anthracene Oil.**—After the separation of the anthracene by allowing the oil to cool in open vessels, the solid constituents are removed, either by filtration or by pressing. The oil thus separated is used for a variety of purposes, such as for impregnating wood, in admixture with creosote oil, as the starting point for the manufacture of carbolineum and similar preparations, and, according to a proposal of Bueb's, as an absorbent for naphthalene in the manufacture of illuminating gas.

The residual crude anthracene is further dried, either in a hydraulic press or centrifuge, to remove adhering oil, when a product containing from 30 to 50 per cent. of pure anthracene is obtained, which is further purified by a variety of alternative processes up to a content of from 70 to 80 per cent. of pure anthracene.

#### VII.—PITCH

**Properties.**—Coal tar pitch is a resinous mass of a dark black colour with a more or less brilliant, conchoidal fracture. Its brittleness varies according to the degree of hardness obtained in the distillation. Accordingly its specific gravity varies from 1.275 to 1.300, while its softening and melting points are still more variable. The specific gravity also depends on the origin of the tar; that of water gas tar pitch does not exceed 1.20, that of vertical retort gas tar pitch and of coke oven tar pitch 1.25 to 1.275, and that of gas tar pitch, as a rule, 1.30 to 1.33. The commercial products are:—Soft Pitch, Medium Hard Pitch, and Hard Pitch, which have the following properties respectively:—

*Soft Pitch* softens at 40° and melts at 50°; it is tough at ordinary temperatures, and can only be broken up at a low temperature, and on long standing the fragments coalesce. The fractured surface shows a brilliant lustre. If left exposed to the sun it soon flows, forming a viscous mass with a mirror-like surface.

*Medium Pitch* (Briquette pitch) softens at 60° and melts at about 70°; it is solid at ordinary temperatures and is easily broken into fragments which, however, rarely show sharp edges. It soon forms a shapeless mass if exposed to sunshine.

*Hard Pitch* begins to soften at 80° to 85° and melts between 95° and 100°. When broken up it forms sharp-edged, resonant fragments of dull lustre which are little affected by exposure to the sun.

Numerous investigations have been made of the elementary composition of pitch. Habets,<sup>1</sup> found in hard pitch of good quality:—

Carbon . . . . .	75.32
Hydrogen . . . . .	8.90
Oxygen . . . . .	16.06
Ash . . . . .	0.43
	<hr/> 100.71 <hr/>

<sup>1</sup> Cf. Gnehl, *Steinkohlenbriquette*, p. 23.



Constam and Rougeot,<sup>1</sup> however, in the course of a comprehensive study of the valuation of coal briquettes and of briquette tar, found the following values:—

	Soft Pitch.	Medium Hard Pitch (Briquette Pitch).
	Per cent.	Per cent.
C . . . .	91.60	85.14 to 92.59
H . . . .	4.89	4.85 " 4.60
O+N+S . .	3.20	7.87 " 2.77
Ash . . . .	0.31	2.54 " 0.04

Donath and Asriel<sup>2</sup> found in:—

	Carbon.	Hydrogen.
Soft pitch . . . . .	91.80	4.62
Medium pitch . . . . .	94.32	2.98
Hard pitch . . . . .	93.16	4.36

Definite relations, such as might be expected, do not, therefore, exist between the hardness and the elementary composition. It is doubtful whether the samples of pitch analysed by Donath and Asriel were derived from the same tar.

According to the investigations of Constam and Rougeot, the heat of combustion of pitch varies from 8100 to 8900 calories, and its calorific value from 7850 to 8650 calories.

If heated in an open crucible, pitch melts and intumesces, and gives off yellow vapours which have a pungent odour, while a porous coke remains. The quantity of coke (which depends on the content of non-volatile carbon) may vary within the limits of 30 to 60 per cent.

Pitch is more or less readily soluble in the usual solvents, less readily soluble in methyl and ethyl alcohols, readily soluble in ether and light petroleum, very readily in chloroform, carbon bisulphide, and benzene, and most completely and quickly soluble in aniline and in the mixture of pyridine bases. These solutions are either brown or black, and exhibit, in reflected light, the characteristic property of bluish green fluorescence of different shades of colour, according to the solvent employed.

A more or less considerable carbonaceous residue remains undissolved, the so-called free carbon (from coke oven and vertical retort tar pitch 5 to 10 per cent., from gas tar pitch 25 to 40 per cent.), the composition of which, according to Behrens<sup>3</sup> and also Donath and Margosches,<sup>4</sup> is as follows:—

<sup>1</sup> Glückauf, 1906, 42, 481; *J. Soc. Chem. Ind.*, 1906, 25, 631, 1873.

<sup>2</sup> *Chem. Rev. Fett. Ind.*, 1903, 10, 54.

<sup>3</sup> *Dingl. polyt. J.*, 1873, 208, 371.

<sup>4</sup> *Chem. Ind.*, 1904, 27, 220; *J. Soc. Chem. Ind.*, 1904, 23, 541.

	Behrens.		Donath and Margosches.
	I. per cent.	II. per cent.	per cent.
Carbon . . . .	90.84	91.92	89.20
Hydrogen . . . .	3.06	3.16	2.30
Nitrogen . . . .	—	—	0.70
Ash . . . . .	0.40	0.87	0.67

**Composition.**—Pitch consists of the non-volatile substances (free carbon, ash) and of the most difficultly volatile substances contained in the tar. Bituminous constituents which decompose on distillation are also present. Carnelly<sup>1</sup> isolated two distinct bitumens of pitch-like appearance, of which one boiled at 427° to 439° and is readily soluble in benzene and carbon bisulphide, while the other distils above 439°, is hardly soluble in benzene, but more readily in carbon bisulphide.

The chemical nature of these substances has not yet been elucidated.<sup>2</sup>

Besides the above substances, pitch contains anthracene, phenanthrene, chrysene, pyrene, acridine, etc., which can be separated by distillation, when the bituminous constituents of the pitch undergo partial decomposition, with the formation of viscous, heavy oils and red, resinous substances.

**Method of Examination.**—The examination of pitch as an intermediate product is carried out according to the methods described later for the examination of the Final Products (p. 836).

**The Working up of Pitch.**—In most cases the tar is distilled for a hard pitch in order to recover as much as possible of the more valuable oils. The further working up of pitch consists in adjusting it for medium or soft pitch or in manufacturing therefrom prepared (regenerated) tar, by adding oil distillation residues; this product is used for various purposes (roofing composition, steel works tar, etc.), and is made up according to requirements with certain specified melting points, specific gravity, consistence, etc.

## C. FINAL PRODUCTS

### I.—COMMERCIAL BENZOL

Commercial benzol is used for very various technical purposes, and is accordingly supplied by tar distilleries in various states of quality and purity. The greatest consumption is in the aniline colour industry; considerable quantities of 90 per cent. benzol are used for carburetting illuminating and water gas, and it also finds increasing application as a liquid illuminant (addition to methylated spirit for incandescent

<sup>1</sup> *J. Chem. Soc.*, 1880, 37, 714.

<sup>2</sup> *Cf. Kraemer, Ber.*, 1903, 36, 645.

lighting (Denayouze and Fernholtz's benzol lamp). The india-rubber and varnish industries use considerable quantities, particularly of heavy benzols (solvent naphtha) as a solvent and as a turpentine substitute respectively. The use of benzene, and especially that of its higher homologues, for the motive power of explosion engines, is also increasing; its effective value is approximately equal to that of the petrol it replaces, and considerably exceeds that of methylated spirit. In these directions there is still a wide field for its employment. Recently, 90 per cent. benzol has been employed to denature spirit for industrial purposes.

The specifications of the quality of commercial benzol vary according to the purpose to which it is to be applied. The conditions relate to the limits of boiling points, the sp. gr. at 15°, the behaviour towards sulphuric acid and bromine, the content of paraffins, thiophene, and carbon bisulphide, as well as to colour and odour, the latter especially in the case of the higher boiling benzols.

The following are the usual commercial products, with their approximate boiling points:—

Commercial Product.	Limits of Boiling Point.	Specific Gravity. 15° 15°
90 per cent. Benzol . .	To 100° 90 per cent., to 120° 100 per cent.	0·880 to 0·888
50 " " . .	{ " 100° 50 " 120° 90 " and to 130° 100 per cent. }	0·878 " 0·880
30 " " . .	" 100° 30 per cent., to 120° 90 per cent.	0·875
0 " " . .	" 100° 0 " 120° 90 " "	0·870 " 0·872
Pure Benzene . .	95 per cent. within 0·8° . . . .	0·883 " 0·885
Thiophene-free Benzene .	95 " " 0·8° . . . .	0·883 " 0·884
Toluene . .	95 " " 0·8° . . . .	0·870 " 0·871
Xylene . .	To 136° 0 per cent., to 140° 90 per cent.	0·867 " 0·869
Cumene . .	" 163° 0 " . to 172° 90 " "	0·886 " 0·890
Pseudocumene . .	" 167° 0 " . to 170° 90 " "	0·888 " 0·890
Solvent Naphtha I. .	" 130° 0 " . to 160° 90 " "	0·870 " 0·880
" " II. .	" 145° 0 " . to 175° 90 " "	0·880 " 0·910
Heavy Benzol . .	" 160° 0 " . to 195° 90 " "	0·920 " 0·945

The proportion of pure benzene in "90 per cent. benzol" may vary considerably (from 60 per cent. to 80 per cent.) with the percentage of impurities present, by which also the specific gravity may be considerably affected. Thus, English benzols are liable to contain a considerable quantity of carbon bisulphide, which will raise the specific gravity proportionately. On the other hand, Scotch benzols contain but little carbon bisulphide but a relatively large amount of light hydrocarbons of the fatty series, which will lower the specific gravity. A good sample of "90 per cent. benzol" should not commence to distil before 80°, or yield more than 20 to 30 per cent. of distillate under 85°.

The composition of commercial benzol is approximately as follows (F. Frank<sup>1</sup>):—

	90 per cent. Benzol.	50 per cent. Benzol.	0 per cent. Benzol.	Solvent Naphtha to 180°.	Solvent Naphtha to 175°.	Heavy Benzol.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Benzene . . . . .	84	43	15	...	...	...
Toluene . . . . .	13	46	75	5	...	...
Xylene . . . . .	3	11	10	70	35	5
Cumene . . . . .	...	...	...	25	60	80
Neutral Naphthalene Oil .	...	...	...	...	5	15

Cumarone and indene are not accounted for in this table; the latter is contained in the heavy benzol up to 40 per cent., and also to about 6 per cent. in the slightly washed naphtha, boiling up to 175°. Further, the proportion of paraffins, carbon disulphide, thiophene, etc., is also not included.

As an average of many years' observations, Kraemer and Spilker<sup>2</sup> give the composition of commercial benzols used in colour works as follows:—

	90 per cent. Benzol.	50 per cent. Benzol.	0 per cent. Benzol.	Remarks.
	Per cent.	Per cent.	Per cent.	
Water . . . . .	0·060	...	...	The water in 90 per cent. Benzol is usually found in summer only, and then only shortly after its manufacture.
Paraffins . . . . .	0·100	0·25	0·50	
Carbon bisulphide . . . . .	0·686	0·39	...	
Compounds absorbing bromine	1·202	1·23	0·82	
Thiophene (in above) . . . . .		(0·264 per cent.)		
Benzene . . . . .	80·922	45·37	13·54	
Toluene . . . . .	14·850	40·32	73·42	
Xylene . . . . .	2·180	12·44	11·69	

The range of boiling points of the commercial products given in the above tables, at the normal pressure of 760 mm. is as follows:—

	Per cent.		Per cent.
90 per cent. Benzol 81·0 to 85°	— 43·0	30 per cent. Benzol 101 to 105°	— 11·0
„ 90°	— 78·0	„ 110°	— 49·0
„ 95°	— 87·5	„ 115°	— 79·0
„ 100°	— 91·5	„ 119·5°	— 90·0
50 per cent. Benzol 78·0 to 90°	— 3·0	„ 120°	— 91·0
„ 95°	— 31·0	„ 125°	— 95·0
„ 100°	— 52·0	0 per cent. Benzol 125 to 130°	— 30·0
„ 105°	— 67·0	„ 135°	— 60·0
„ 110°	— 77·0	„ 140°	— 87·0
„ 115°	— 84·0	„ 141·5°	— 90·0
„ 120°	— 90·0	Solvent Naphtha I. 135 to 140°	— 20·0

<sup>1</sup> *Chem. Ind.*, 1901, 24, 239.

<sup>2</sup> Muspratt, *Handbuch der technischen Chemie*, 4th ed., 8, pp. 33 et seq.

	Per cent.		Per cent.
Solvent Naphtha I. 140 to 145°	— 50.0	Pure Benzene . 79.5 to 79.6°	— 2.0
„ 150°	— 75.0	„ 79.8°	— 6.0
„ 155°	— 85.0	„ 80.0°	— 10.0
„ 159°	— 90.0	„ 80.1°	— 65.0
„ 160°	— 91.0	„ 80.2°	— 94.0
Solvent Naphtha II. 147 to 150°	— 5.0	Toluene . 110.2 to 110.3°	— 15.0
„ 155°	— 25.0	„ 110.4°	— 35.0
„ 160°	— 50.0	„ 110.5°	— 70.0
„ 165°	— 72.0	„ 110.6°	— 90.0
„ 170°	— 84.0	„ 110.7°	— 95.0
„ 173°	— 90.0	Cumene . 165 to 166°	— 7.0
„ 175°	— 91.0	„ 168°	— 37.0
Heavy Benzol . 160 to 165°	— 15.0	„ 170°	— 70.0
„ 170°	— 45.0	„ 172°	— 90.0
„ 175°	— 70.0	Pseudocumene . 166 to 167°	— 30.0
„ 180°	— 82.0	„ 168°	— 90.0
„ 187°	— 90.0	„ 168.5°	— 95.0
„ 190°	— 91.0		

### (a) Determination of the Specific Gravity.

The determination of the specific gravity, which is often quoted in the valuation of commercial benzol, is carried out in the usual way. It should, however, be pointed out that the specific gravity of a benzol is no reliable criterion as to its nature, since it is markedly influenced by the character of the impurities present. If amongst the latter the specifically heavier carbon disulphide predominates, the specific gravity will be higher than when the lighter hydrocarbons form the major portion of the impurities, and, again, the specific gravity may be approximately normal if both classes of compounds are present together in such proportion that their effects are neutralised.

### (b) Determination of the Range of Boiling Point.

For the valuation of a commercial benzol by the determination of its range of boiling point, it is necessary, in order to obtain comparative results, that the distillation should be conducted under rigid and exactly specified conditions. In this country most commercial contracts are based upon Allen's "Retort Test,"<sup>1</sup> which is described by its author as follows:—

One hundred c.c. of the sample (say a 90 per cent. benzol) is measured in an accurately graduated cylinder and poured thence into a tubulated retort, of such a size as to be capable of containing 200 c.c. when placed in the ordinary position for distillation. The retort should be previously rinsed with some of the sample to be tested. A delicate thermometer is fitted in the tubulure of the retort by a cork, so that it may be vertical and the lower end of the bulb be  $\frac{3}{8}$  in. distant

<sup>1</sup> *Commercial Organic Analysis*, 3rd ed., vol. ii., part ii., p. 184.

from the bottom of the retort. The thermometer should be 14 in. long, and its bulb sufficiently small to ensure complete immersion in the liquid. The first division on the stem should be at  $70^{\circ}$ , which point should be well out of the tubulure of the retort, and the graduation should be continued in tenths of a degree up to  $130^{\circ}$ . The neck of the retort is inserted into the inner tube of a Liebig condenser and pushed down as far as it will go. The condenser should be from 15 in. to 18 in. in length, and well supplied with water. No cork or other connection is necessary between the retort neck and condenser tube. The arrangement of the apparatus is shown in Fig. 125. Before use,

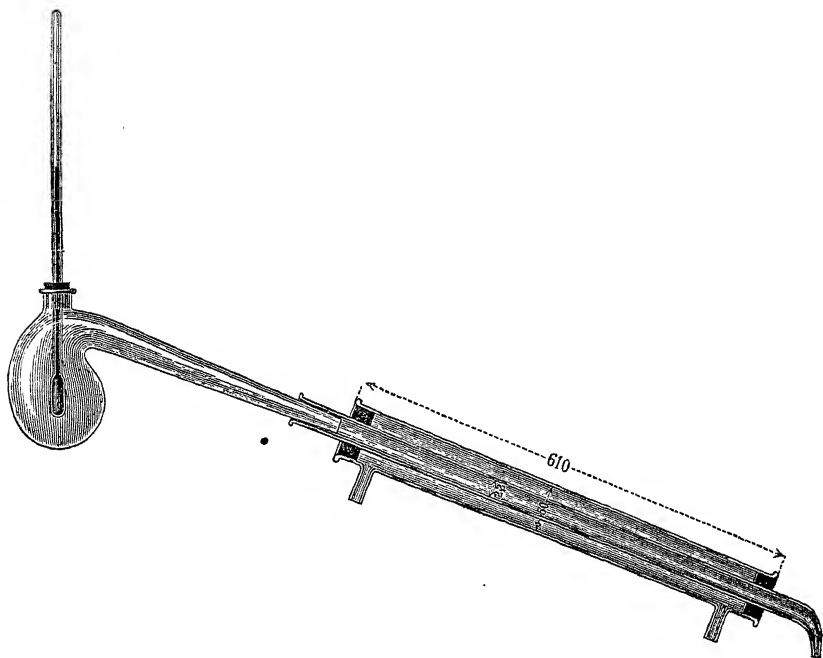


FIG. 125.

the tube of the condenser should be rinsed or sprayed with a little of the sample and allowed to drain. The graduated cylinder employed for measuring out the sample is next placed under the farther end of the condenser tube in such a manner as to catch all the distillate whilst allowing it to drop freely. The retort is then heated by the naked flame of a Bunsen burner, provided with an air-regulator which works automatically with the movements of the tap, and surrounded with a screen to exclude draughts. The flame should be small, about the size and shape of a filbert, and when the distillation of the benzol commences, it must be so regulated that the condensed liquid shall fall

rapidly in distinct drops, but not in a trickle or continuous stream. When distillation begins, the rise of the thermometer is carefully watched. The moment it registers a temperature of  $85^{\circ}$  (or as much below this temperature as will allow the "after-rise" to bring the thermometer to this temperature) the flame is extinguished. Four or five minutes are allowed for the liquid in the condenser to drain into the measuring cylinder, and then the volume of the distillate is read off and recorded. The burner is then relighted and the distillation continued till the thermometer rises to  $100^{\circ}$ , when the gas is turned off as before, and the volume of the distillate read off, after allowing time for draining. The residual liquid in the retort is allowed to cool and is then poured to the last drop into the measuring cylinder. Any deficiency from the 100 c.c. originally taken is regarded as "loss by evaporation or other natural causes," and is to be added to the measure of the distillate collected at each temperature. The corrected volumes are reported as the "strength" of the benzol at the respective temperatures. It is very desirable to observe the barometric pressure before making an experiment. A difference of 1 in. in the height of the barometer makes a difference of  $1^{\circ}$  in the boiling point, and hence if the barometer registers 29.5 in. instead of 30 in. the gas should be extinguished so that the thermometer may show a temperature of  $99^{\circ}.5$  instead of  $100^{\circ}$ .

A more reliable method than the above for the assay of commercial benzols, and which is in general use in Germany, is the result of a proposal due to Lunge<sup>1</sup> for the attainment of uniform methods of analysis.

It is based upon the employment of an apparatus proposed by

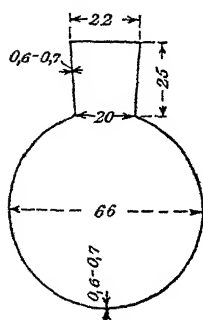


FIG. 126.

Bannow in 1886, and makes use of the results obtained by Lenders<sup>2</sup> on the influence of the height of the barometer upon the boiling point of benzene hydrocarbons. The apparatus for carrying out the distillation, as described by Kraemer and Spilker,<sup>3</sup> is shown in Figs. 126 and 127. A spherical vessel (Fig. 126) made of strong copper 6 to 7 mm. thick, which is slightly flattened at the bottom, is used for the distillation. It has a neck 25 mm. long, the diameter of which is 22 mm. at the top and 20 mm. at the bottom, for the reception of the glass prolongation, which is 150 mm. long and 14 mm. wide. In the middle of the glass portion is a bulb of 30 mm. diameter, above which, at a distance of 10 mm., a side-tube of 8 mm. diameter is sealed almost at right angles. The glass column and the spherical vessel are

<sup>1</sup> *Chem. Ind.*, 1884, 7, 50.

<sup>2</sup> *Ibid.*, 1889, 12, 169.

<sup>3</sup> Muspratt, *Handbuch der technischen Chemie*, 4th ed., 8, p. 35.

connected by means of a good cork stopper. A Bunsen burner of about 7 mm. diameter or a benzene spirit lamp is used for heating. The burner is placed in a tinplate cylinder provided with a door, and also with four round holes 10 mm. above the bottom, and four more 10 mm. below the top, for ventilation (Fig. 127). This small heater is covered at the top with a sheet of asbestos having a round hole of 50 mm. diameter in which the spherical retort is placed. The inner tube of the glass Liebig condenser has a length of 800 mm., and is inclined with the outlet 100 mm. below the level of the inlet. The thermometer is made of thin glass, and is graduated in  $\frac{1}{10}$ ths of a degree for pure benzene, and in  $\frac{1}{5}$ ths of a degree for commercial products; it should be about one-half the diameter of the neck, and must be so fixed that its bulb is exactly in the middle of the widened part,

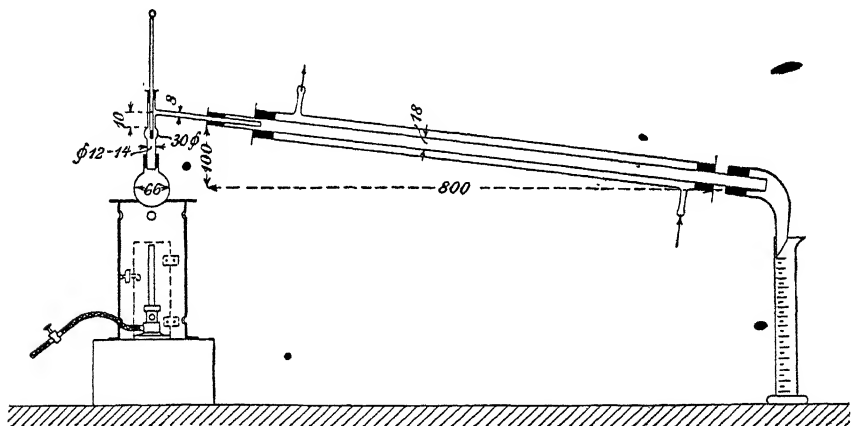


FIG. 127.

and should be compared from time to time with a standard thermometer. The distillate leaves the condenser through a bent adapter, and runs down the sides of a 100 c.c. graduated cylinder.

To carry out the valuation, 100 c.c. of the liquid are put into the flask, and the distillation is conducted so that 5 c.c. distil over per minute, *i.e.*, two drops per second; it is complete when 95 c.c. have distilled over. In order to correct any cause of error due to different barometer readings, the method of Bannow can be employed, in which the thermometer reading is checked by distilling 100 c.c. of water in the same vessel, and observing the thermometer reading at the boiling point of the water, when 60 c.c. of the water have distilled over. It is simpler; however, to utilise Lender's corrections as follows:—

1. When the barometer stands at 720 to 780 mm. the percentages of the distillate obtained are reduced to the corresponding amounts



for the normal reading of 760 mm. by applying the following corrections:—

For 90 per cent. benzol, 0.033 per cent.,  
for 50 per cent. „ 0.077 „  
to be added or subtracted for each millimetre of difference.

2. For barometer readings of from 720 to 780 mm. for distillation up to 100°, for each millimetre difference add or subtract:—

For 90 per cent. benzol, 0.0453°,  
for 50 per cent. „ 0.0461°.

3. In the case of pure products, the difference of temperature for each millimetre difference in the barometer readings between 720 mm. and 780 mm. is:—

Benzene, about 0.043°,  
Toluene, „ 0.047°,  
Xylene, „ 0.052°.

*Example.*—In the case of a 90 per cent. benzol, 88.8 per cent. distilled over at 100°, the barometer reading being 721.2 mm.; to reduce the percentage to the standard reading of 760 mm.:—

$$\begin{aligned} 760 - 721.2 &= 38.8 \text{ mm.} \\ 38.8 \times 0.033 &= 1.28 \text{ per cent.} \\ 88.8 - 1.28 &= 87.52 \text{ „} \end{aligned}$$

at 100°.

Or, if the distillation of the same benzol be carried out at 730 mm. barometer reading, then according to 2:—

$$\begin{aligned} 760 - 730 &= 30 \text{ mm.} \\ 30 \times 0.0453 &= 1.359°. \end{aligned}$$

In carrying out this distillation, therefore, in order to obtain the percentage distilled over, when the height of the barometer is 760 mm., the temperature of distillation must be taken at  $100 - 1.359 = 98.641$ , or approximately 98°6, instead of 100°.

A. Spilker has shown, however, that the following artificially prepared mixtures all give the limits of boiling point required for a 90 per cent. benzol:—

- (a) 82.0 per cent. benzene + 18.0 per cent. toluene.
- (b) 92.2 „ „ + 7.8 „ „ xylene.
- (c) 90.0 „ „ + 5.0 „ „ toluene + 5.0 per cent. xylene.
- (d) 84.0 „ „ + 13.0 „ „ + 3.0 „ „

Of these mixtures only (a) corresponds in composition to an average commercial 90 per cent. benzol.

## (c) Estimation of Individual Benzene Hydrocarbons.

The quantitative estimation of the benzene, toluene, and xylene contained in commercial benzols is carried out by fractional distillation. This is easily done as the boiling points of the separate constituents lie far apart:—Benzene,  $80^{\circ}2$ ; toluene,  $110^{\circ}9$ ; xylene,  $138^{\circ}$  to  $142^{\circ}$ . For this purpose an apparatus is used similar to a technical distilling column. H. Kreis<sup>1</sup> compared the efficiency of various forms of glass apparatus of this kind, especially for mixtures of benzene and toluene, and came to the conclusion that a simple Hempel column was quite as effective as the complicated apparatus of Le Bel-Henninger; the subject has since been more fully investigated by Young (cf. *infra*). Monnet's<sup>2</sup> apparatus, shown in Fig. 128, is of similar type to the Hempel tube; it separates mixtures of liquids almost as completely as the large scale rectifying columns of the Savalle type. The glass column D, 0.35 to 0.40 metres long, and of 28 to 35 mm. bore, is filled with metallic granules or with pieces of glass or flint; the bottom of the tube is contracted to 5 mm. diameter so that it can be introduced through the cork of the flask B. Above the narrow portion is a funnel with a fluted rim so that the condensed liquid flows back to B, whilst the contents of D are kept in place. Lead-shot is the most convenient material to use. The tube is filled to half its height with small shot upon which is placed a layer of copper gauze, and the rest of the tube is filled with larger shot to about 25 mm. below the side tube J, which leads to a Liebig condenser, and is placed 5 or 6 cm. below the top of the column. The thermometer bulb is placed immediately above the metal shot, without touching it. The heating of the liquid up to the point where regular distillation begins must be carefully conducted. When used for easily condensible liquids, such as high-boiling hydrocarbons, aniline, toluidine, etc., the flask B is preferably covered with wire gauze, and the column with thick asbestos sheet, in order to hinder radiation. The fractionating efficiency of the apparatus is, on the whole, proportional to the total surface and conductivity of the metallic filling.

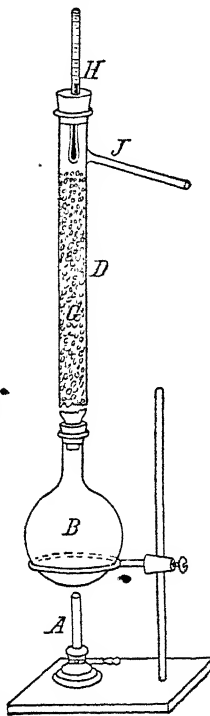


FIG. 128.

A valuable comparison of the relative efficiency of various forms of still-heads or fractionating columns has been made by Young,<sup>3</sup> who has also designed several new forms of fractionating columns, which are

<sup>1</sup> *Annalen*, 1889, 254, 259.<sup>2</sup> *Monit. Scient.*, 1887 [4], 335, 835.<sup>3</sup> *J. Chem. Soc.*, 1899, 75, 679; cf. also S. Young, *Fractional Distillation*, 1903.

shown in Fig. 129; they are known as the "Pear," the "Rod and Disc," and the "Young and Thomas" forms.

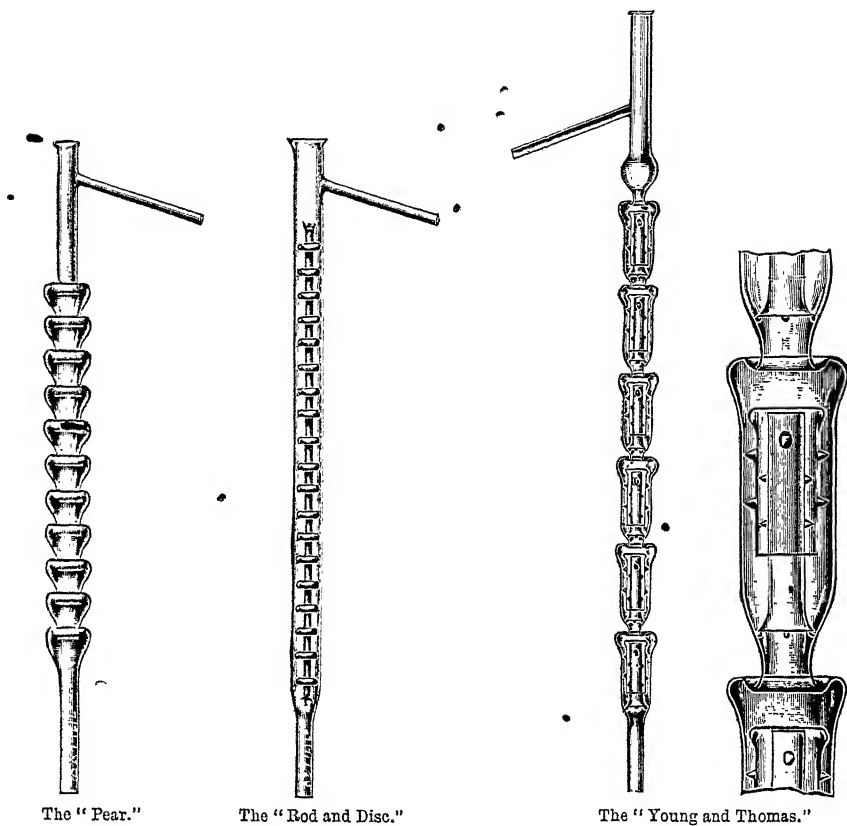


FIG. 129.

The following table gives the results of a single distillation of a mixture of equal weights of pure benzene (boiling point  $80^{\circ}2$ ) and

Temperature Range.	Ordinary Distillation Bulb.	Hempel Column.	"Rod and Disc" Column (20 Discs).	"Pear" Column (18 Pears).	Le Bel-Henninger Column (8 Bulbs).	Young and Thomas Column (18 Sections).
$80^{\circ}2$ to $81^{\circ}2$	None	} 20.6 {	None	None	None	31.5
$81^{\circ}2$ ,, $83^{\circ}2$	None		2.0	3.0	0.5	7.3
$83^{\circ}2$ ,, $107^{\circ}9$	82.4		64.7	59.4	68.9	14.4
$107^{\circ}9$ ,, $110^{\circ}3$	6.8		7.4	5.0	9.8	4.0
$110^{\circ}3$ ,, $110^{\circ}9$	5.9		7.5	11.0	6.8	8.1
Residue	4.2	24.9	18.4	21.6	14.0	34.7

pure toluene (boiling point  $110^{\circ}9$ ) with different fractionating columns. The distillate was collected in each case in eleven fractions at intervals of about  $3^{\circ}$ , the residue after the boiling point of toluene had been

reached forming a twelfth fraction. The same rate of distillation (one drop per second) was maintained throughout, as it was found that this factor has a marked influence on the efficiency of the separation.

Fifty grams of the mixture were distilled in each case, and the distillates at each temperature are given in percentages.

The remarkable efficiency of the Young and Thomas still-head is shown by the fact that in a single distillation over 70 per cent. of the benzene and toluene present are separated in an almost pure condition. From the figures given an idea may be formed of the number of fractionations which will be necessary with each form of apparatus to obtain a complete separation into pure products.

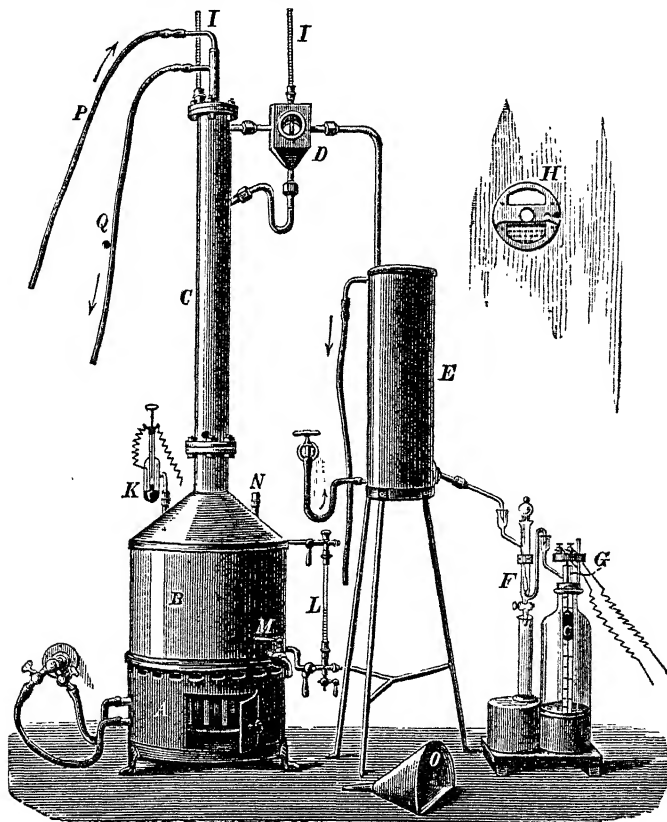


FIG. 130.

Many tar-products and colour works laboratories employ the small distilling column of Claudon and Morin,<sup>1</sup> which is constructed on the same model as the larger columns in technical use.

The apparatus (Fig. 130) is heated by a burner, A, with two heating rings, which are supplied separately with gas. The still B has its

<sup>1</sup> *Bull. Soc. Chim.*, 1887, 48 (2), 804.

bottom slightly inclined towards the outlet cock M, and is connected with the column C, the analyser D, and the condenser E. The still is also provided with a gauge glass, L, and supply tube, N, into which the funnel O fits. There is also an electric pressure indicator, K, which rings an alarm bell when the pressure exceeds a certain limit; the contact consists of mercury, which also serves as a seal. The column C contains ten plates, H, similar to those in large distilling columns. They are easily cleaned and the copper gauze is easily replaced. The projecting inner tube I is supplied through P with cooling water which is led away through Q. The analyser D is provided with observation windows and a thermometer, Z, and causes the spray or foam which is mechanically carried over to flow back into the column. The condenser E is of the usual pattern; F is a tube and hydrometer for determining

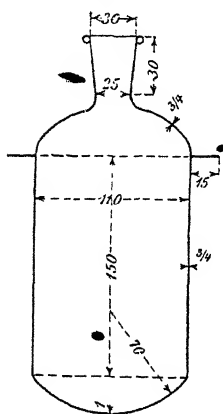


FIG. 181.

the specific gravity of the distillate, and also for taking samples of the liquid from the bottom cock before it flows into the receiver G. As the latter is filled it raises a float, c, which finally makes electric contact and rings a bell, when another receiver is placed in position. The apparatus must be heated up slowly at first, so that the plates of the column may be filled and the cooling water regulated; the heat supply is then gradually increased until regular distillation commences.

According to Frank, and also according to Kraemer and Spilker,<sup>1</sup> the rectification test is carried out by general agreement in a copper still of the form and dimensions shown in Fig.

131, 1 kg. of benzol being used, and the vapour passed through a Le Bel-Henninger column 60 cm. long. The thermometer, the position and diameter of the condenser, and the rate of distillation are the same as described on p. 784; the distillate is, however, collected in tared flasks and weighed.

Whatever the nature of the apparatus used, the single fractions should be collected as follows:—

*For 50 and 90 per cent. Benzol.*

Up to 79° = First runnings.  
79° „ 85° = Benzene.  
85° „ 105° = Mixed fraction.  
105° „ 115° = Toluene.  
Remainder = Xylene.

*For Pure Benzene.*

Up to 79° = First runnings.  
79° „ 81° = Benzene.  
Remainder = Last runnings.

*For Toluene.*

Up to 109° = First runnings.  
109° „ 110°·5 = Toluene.  
Remainder = Last runnings.

*For Xylene.*

Up to 135° = First runnings.  
135° „ 137° = *p*-Xylene.  
137° „ 140° = *m*-Xylene.  
140° „ 145° = *o*-Xylene.  
Remainder = Last runnings.

<sup>1</sup> *Loc. cit.*

Employing this procedure, ordinary commercial benzols give the following average figures:—

	90 per cent. Benzol.	50 per cent. Benzol.
First runnings . . . .	1.0 per cent.	0.3 per cent.
Benzene . . . . .	78.8 "	18.3 "
Middle fraction . . . .	10.0 "	47.5 "
Toluene . . . . .	8.0 "	23.7 "
Xylene . . . . .	2.0 "	10.0 "
Loss on distillation . .	0.2 "	0.1 "
	Pure Benzene.	Toluene.
First runnings . . . .	0.5 per cent.	0.3 per cent.
Benzene . . . . .	98.0 "	
Toluene . . . . .	— "	97.3 "
Last runnings . . . .	1.2 "	2.2 "
Loss on distillation . .	0.3 "	0.2 "

*Xylol.*

First runnings . . . .	1.3 per cent.
<i>p</i> -Xylene . . . . .	15.0 "
<i>m</i> -Xylene . . . . .	76.5 "
<i>o</i> -Xylene . . . . .	5.0 "
Last runnings . . . .	2.0 "
Loss on distillation . .	0.2 "

The separation of the three xylene isomers:—

<i>p</i> -Xylene, boiling point . . . . .	138°.5
<i>m</i> -Xylene, boiling point . . . . .	140°
<i>o</i> -Xylene, boiling point . . . . .	142°

cannot, of course, be completely effected by fractional distillation, but the test is nevertheless of some assistance in estimating the value of a technical xylol, as the three isomers differ in commercial utility. According to O. Jacobsen,<sup>1</sup> commercial tar xylol consists of 70 to 75 per cent. of *m*-xylene, 20 to 25 per cent. of *p*-xylene, and 10 to 15 per cent. of *o*-xylene; its composition varies with the nature of the tar, from which it is produced. It also contains up to 10 per cent. of ethylbenzene,<sup>2</sup> and considerable quantities of paraffin-like substances, which are not attacked by fuming sulphuric acid.

Noelting has given a method of separation, depending upon the fact that *o*- and *m*-xylene are sulphonated by cold, concentrated sulphuric acid and converted into sulphonic acids, the sodium salts of which can be separated by their different solubility in water; *p*-xylene, on the other hand, is scarcely attacked by concentrated sulphuric acid even on heating, and is only sulphonated and dissolved by slightly fuming acid. After the latter treatment the admixed paraffins remain behind and can be weighed.

<sup>1</sup> *Ber.*, 1877, 10, 1009; 1881, 14, 2628.

<sup>2</sup> Noelting and Palmer, *ibid.*, 1891, 24, 1955.

Levinstein<sup>1</sup> has worked out methods for the estimation of the three xylenes in commercial xylol, based upon the above reactions and also upon the observation that *m*-xylene is scarcely attacked by hot, dilute nitric acid, whilst *o*- and *p*-xylene are oxidised to the respective toluic acids or their nitro-derivatives. In order to estimate the *m*-xylene, 100 c.c. of the crude xylol is heated for a half to one hour in a flask on a sand-bath with a mixture of 40 c.c. of nitric acid of sp. gr. 1.4 and 60 c.c. of water. When red fumes cease to be evolved the residual hydrocarbon is separated and freed from toluic acids, either by repeated washing with sodium hydroxide solution or by distilling from the latter with steam. The hydrocarbon obtained consists of *m*-xylene mixed with paraffins. The latter remain undissolved on shaking the mixture with one and a half times its volume of concentrated sulphuric acid for half an hour, and the diminution in volume gives the *m*-xylene present. To obtain the percentage of *p*-xylene, 100 c.c. of the crude xylol is shaken for half an hour, or until further solution ceases, with 120 c.c. of concentrated sulphuric acid (sp. gr. 1.85), keeping the mixture cool. Upon allowing to settle, the unaltered hydrocarbons (*p*-xylene and paraffins) rise to the top and are measured. By deducting the volume of the paraffins, which is found by heating the mixture with an equal volume of fuming sulphuric acid containing 20 per cent. of SO<sub>3</sub>, the quantity of *p*-xylene present is obtained. The percentage of *o*-xylene is ascertained by difference, or by fractional separation of the *o*-xylene sodium-sulphonate from the product of sulphonation with ordinary sulphuric acid. Levinstein gives the following analyses of a number of Scotch and English xylols effected by the above method.

Sample.	Origin.	Sp. Gr. at 19°.	Boiling Point.	Meta- Xylene.	Para- Xylene.	Ortho- Xylene.	Paraffins.
A.	Pure <i>m</i> -Xylene from English Crude Xylol	0.8668	142° to 143°	Per cent. 100	Per cent. 0	Per cent. 0	Per cent. 0
B.	English (Manchester Tar)	0.8629	134° „ 140°	87	6	4	3
C.	„ „ „	„	140° „ 143°	87	4	6	3
D.	„ „ „	„	141° „ 145°	83	5	7	5
E.	„ „ „	0.8660	138° „ 141°	79	3	15	3
F.	Scotch „ „	0.8574	134° „ 141°	72	8	12	8
G.	Unknown „ „	„	139° „ 141°	70	5	15	10
H.	Mixed „ „	0.8605	134° „ 141°	81	10	3	6
I.	„ „ „	„	136° „ 142°	86	6	4	4
J.	„ „ „	0.8613	136° „ 141°	86	6	2	6
K.	„ „ „	„	140° „ 141°	86	3	5	6
L.	„ „ „	0.8600	136° „ 142°	85	6	3	6

According to A. Reuter<sup>2</sup> this method is valueless, as contrary to the statements of Noelting, Witt, and Forel,<sup>3</sup> it gives much too low a result for *p*-xylene. Reuter<sup>4</sup> has himself suggested a method based upon the

<sup>1</sup> *J. Soc. Chem. Ind.*, 1884, 3, 77.

<sup>2</sup> *Ber.*, 1884, 17, 2028.

<sup>3</sup> *Ibid.*, 1885, 18, 2068.

<sup>4</sup> *Chem. Zeit.*, 1889, 13, 830, 850.

fact that sulphuric acid of slightly more than 80 per cent. strength acts upon *m*-xylene to form a sulphonic acid, but has no action on *o*- and *p*-xylene; and that on sulphonating the remaining mixture of *o*- and *p*-xylene with excess of concentrated sulphuric acid the sulphonic acid of *p*-xylene crystallises out, whilst that of the *o*-xylene remains liquid.

A similar method for the determination of *m*-xylene in commercial xylol has been described by Crafts.<sup>1</sup> Börnstein and Kleemann<sup>2</sup> separate the isomeric xylenes by conversion into the xylidines and by their different behaviour with dry sulphur dioxide. Lastly, Friedel and Crafts<sup>3</sup> have devised a method for the separation of ethyl-benzene from *o*-xylene. O. Jacobsen<sup>4</sup> has described a method of separation of the isomeric trimethylbenzenes, but this is seldom required; it depends upon the different behaviour of their sulphamides towards alcohol.

#### (d) Distinction and Estimation of Coal Tar Benzene in admixture with Petroleum Benzine and Similar Products.

It is frequently necessary to distinguish between the light hydrocarbons of coal tar and those from petroleum, lignite, and shales (benzoline, petroleum ether, cleaning benzine, petrol, etc.). This can usually be done by smell alone, but with more certainty by determining the specific gravity, which is never below 0.867 for coal tar benzols, and seldom exceeds 0.700 for the other products in question. Their different behaviour in the presence of nitro-sulphuric and fuming sulphuric acid is also characteristic, and can be employed for the detection and quantitative determination of any admixture of coal tar benzol with petroleum benzine and similar substances; a comparative table has been given by Allen.<sup>5</sup> According to A. Lainer<sup>6</sup> benzol becomes very turbid when shaken up with traces of alcohol of not more than 95 per cent. strength, whilst benzine remains clear under these conditions. Gawalowski<sup>7</sup> has pointed out that picric acid is almost insoluble in petroleum benzine but dissolves readily in benzene, forming a dark yellow solution. Concentrated solutions of picric acid in benzene are precipitated when added to petroleum benzine. Holde<sup>8</sup> utilises the behaviour of the two classes of hydrocarbons in the presence of coal tar pitch as a test for adulteration of one with the other. He extracts powdered pitch completely with high-boiling petroleum, and after drying preserves it as a reagent. Enough of this to cover the point of a knife is placed on a small filter and 5 c.c. of the liquid to be tested is poured over it. As little as 5 to 10 per cent. of benzene in petroleum

<sup>1</sup> *Comptes rend.*, 1892, 114, 1110.

<sup>2</sup> *Ber.*, 1891, 24, Ref. 486.

<sup>3</sup> *Comptes rend.*, 1885, 101, 1218.

<sup>4</sup> *Ber.*, 1876, 9, 256.

<sup>5</sup> *Chem. News*, 1879, 40, 101.

<sup>6</sup> *Chem. Revue*, 1897, p. 55.

<sup>7</sup> *Chem. Centr.*, 1897, I., 1038.

<sup>8</sup> *Fischer's Jahresber.*, 1895, p. 554.



benzine of sp. gr. 0.64 to 0.70 can be detected by the yellow coloration of the filtrate. By making comparative tests, the approximate quantity of added benzol can be estimated from the intensity of the coloration. Inversely, the quantity of petroleum benzine in benzol can be arrived at by observing the coloration with pitch, and comparison with that given by standard mixtures.

According to E. Valenta,<sup>1</sup> both light and heavy coal tar oils are completely soluble in dimethyl sulphate, whilst petroleum oils are only sparingly soluble or insoluble; Graefe<sup>2</sup> has made use of this reagent for the analytical examination of mixtures of tar oils and mineral oils.

G. Halphen<sup>3</sup> gives particulars for the estimation of benzene in motor spirits (petrol), for which mixtures of benzene and petroleum hydrocarbons are now frequently used. The high specific gravity of such mixtures (0.750 and over) compared with that of petroleum spirit (0.702 to 0.735) at once indicates the presence of benzene.

The method of Kraemer and Böttcher, which is based upon the diminution in volume on shaking the petroleum spirit with a mixture of strong sulphuric acid and fuming sulphuric acid, is inaccurate, owing to simultaneous absorption of olefines and polymerisation of certain hydrocarbons. In Halphen's method of separation, the benzene hydrocarbons are converted into mononitro-derivatives, which are then absorbed by sulphuric acid, and the amount of benzene is calculated from the increase in volume of the acid. In preliminary experiments it was found that the pure petroleum spirit gave apparent yields of benzene in the following proportions:—American petrol, 0.87; Roumanian, 1.74 to 3.48 (7 samples); and Russian, 3.04 per cent. (5 samples). It was, therefore, necessary to subject the samples to a preliminary shaking with an equal volume of sulphuric acid (sp. gr. 1.84) to remove, before the nitration, the bulk of the hydrocarbons capable of absorption by the acid. Ten c.c. of the petroleum spirit thus purified are placed in a flask closed with a stopper pierced with two holes, through one of which passes the stem of a stoppered funnel containing 10 c.c. of fuming nitric acid, whilst a long tube passes through the other. The acid is added 4 or 5 drops at a time, the flask being meanwhile continually shaken and cooled in water, and the shaking is subsequently continued for 5 to 7 minutes. After the nitration is complete 10 c.c. of water are introduced, little by little, through the funnel, whilst the flask is still kept cool, and then 40 c.c. of water, which may be added in one volume, and the flask is well shaken and cooled, so that the nitrous vapours are absorbed. The products of the nitration are now transferred to a separating funnel, the flask

<sup>1</sup> *Chem. Zeit.*, 1906, 30, 266; *J. Soc. Chem. Ind.*, 1906, 25, 366.

<sup>2</sup> *Laboratoriumsbuch für die Braunkohlenteerindustrie*, p. 134.

<sup>3</sup> *Les Matières Grasses*, 1910 (3), 1987; *J. Soc. Chem. Ind.*, 1910, 29, 1447.

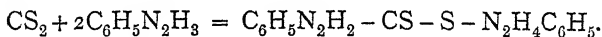
being rinsed out with 10 c.c. of the purified petroleum spirit, and the whole shaken for a few seconds and allowed to stand for 30 minutes. The aqueous layer and any insoluble oil are then drawn off, and the petroleum spirit layer containing the nitro-derivatives in solution is transferred to a stoppered graduated cylinder with a capacity of 30 to 35 c.c., where it is shaken with 5 c.c. of sulphuric acid (sp. gr. 1.83). The cylinder is then allowed to stand for 30 minutes, after which the increase in volume of the acid is noted. This increase, multiplied by 0.87, gives the volume of benzene in the quantity of sample taken.

### (e) The Detection and Estimation of Impurities.

Most of the impurities, especially the hydrocarbons of the fatty series, carbon bisulphide, and thiophene, tend to accumulate, on account of their low boiling point, in the 90 per cent. benzol, whilst others such as indene, cumarone, ethyl benzene, etc., are more frequently found in the higher fractions. The following are the chief methods employed for their detection and determination.

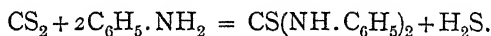
#### 1. Carbon Bisulphide.

This substance is best detected by the phenylhydrazine method of Liebermann and Seyewitz.<sup>1</sup> Ten c.c. of the benzol to be tested are treated with four to five drops of phenylhydrazine, and after repeated shaking, are allowed to stand for one to one and a half hours. A crystalline precipitate of the phenylhydrazine salt of phenylthiocarbazine acid is formed; the reaction takes place according to the equation:—



Even 0.2 per cent. of carbon bisulphide forms a thick magma of crystals, and when 0.03 per cent. is present the reaction is still quite distinct, the smallest detectable amount being about 0.02 per cent. The precipitation may be conveniently hastened by adding a minute crystal of the salt. The test can be made still more delicate by distilling the sample and testing the first portions of the distillate, in which the carbon bisulphide accumulates.

E. Votocek and R. Potmesil<sup>2</sup> test for carbon bisulphide by Hofmann's reaction, the formation of diphenylthiourea according to the equation:—



This reaction occurs rapidly in alkaline solution, and the alkali sulphide which is formed, is readily detected by sodium nitroprusside; the test is quickly carried out, not taking longer than fifteen minutes.

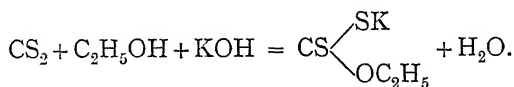
The quantitative determination of carbon bisulphide may also be

<sup>1</sup> *Chem. Zeit.*, 1895, 19, 958.

<sup>2</sup> *Chem. Zeit. Rep.*, 1891, 25 [76], 275.

effected by the method of Liebermann and Seyewitz. For this purpose the reaction is performed in stoppered graduated 10 c.c. cylinders. After standing for several hours, the volume occupied by the crystalline precipitate is compared with that obtained in similarly treated tubes containing standard mixtures of benzene and carbon bisulphide.

The method is rather slow for technical work, and this objection also applies to the ammonium thiocyanate method of Holland and Phillips,<sup>1</sup> and to the very exact method of Goldberg.<sup>2</sup> Frank's method, which depends on A. W. Hofmann's<sup>3</sup> xanthate reaction and the volumetric determination of the carbon bisulphide as insoluble copper xanthate, is in most general use. The reaction takes place according to the equation:—



The estimation is carried out as follows:—Fifty grams of the benzol to be tested is well mixed with 50 g. of alcoholic potassium hydroxide solution (11 g. of potassium hydroxide in 90 g. of absolute alcohol) and allowed to stand for some hours at the ordinary temperature. The whole is then shaken up with about 100 c.c. of water, the aqueous layer separated from the benzene, the latter again washed several times with water, and the washings added to the aqueous solution containing the xanthate. This solution, or an aliquot portion, is then titrated with a solution containing 12.475 g. of copper sulphate crystals per litre, which corresponds to 0.0076 g. of  $\text{CS}_2$  per cubic centimetre. For this purpose, it is neutralised with acetic acid and the copper solution added until a drop of the solution placed on filter paper next to a drop of potassium ferrocyanide solution forms at the point of contact a reddish brown zone of copper ferrocyanide. The end-point is also plainly indicated by the coagulation of the copper xanthate, which at first is finely divided. The above quantity of alcoholic potassium hydroxide solution is sufficient if less than 5 per cent. of carbon bisulphide is present, this being the case with 90 per cent. and 50 per cent. benzols, which contain on the average from 0.2 to 1.0 per cent., and from 0.0 to 0.5 per cent. respectively. Benzol first runnings, on the other hand, often contain considerably more than 5 per cent. of carbon bisulphide, in which case the quantity of benzol used must be reduced or more alcoholic potash employed. Higher boiling benzols do not contain the bisulphide.

If the amount of total sulphur only is required, without regard to

<sup>1</sup> *J. Soc. Chem. Ind.*, 1884, 3, 296.

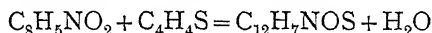
<sup>2</sup> *Z. angew. Chem.*, 1899, 12, 75.

<sup>3</sup> *Ber.*, 1880, 13, 1732; cf. also Nickels, *Chem. News*, 1881, 43, 148; Biehinger, *Dingl. polyt. J.*, 1890, 276, 78; *J. Gasbeleucht.*, 1890, 33, 341; Schmitz-Dumont, *Chem. Zeit.*, 1897, 21, 487, 510; Frank, *Chem. Ind.*, 1901, 24, 262.

the form in which it is present, the methods used in the mineral oil industry may be employed. Irwin<sup>1</sup> has suggested a special method for this determination.

## 2. Thiophene.

A characteristic reaction for the detection of thiophene in benzol is the coloration produced by isatin and sulphuric acid, first observed by Laubenheimer. In the case of thiophene this is a beautiful blue ("Indophenine"), in the case of thiotolene it is blue with a reddish tinge, and with thioxene, reddish violet. The reaction



is carried out as follows:—Several cubic centimetres of pure sulphuric acid are poured over a few pieces of isatin and placed in a shallow porcelain dish, which has previously been rinsed out with pure sulphuric acid. A layer of benzol is then poured over the acid, covered with a watch-glass, and allowed to stand. If the benzol is pure, no blue rings will form round the isatin within an hour. Further particulars of this test are given by F. W. Bauer,<sup>2</sup> Storch,<sup>3</sup> and Liebermann and Pens.<sup>4</sup>

Liebermann<sup>5</sup> recommends nitroso-sulphuric acid or amyl nitrite and sulphuric acid as a sensitive reagent for thiophene. A suitable reagent can be prepared by stirring 8 per cent. of sodium nitrite into pure concentrated sulphuric acid, and allowing it to stand in an open vessel until it has absorbed 6 to 7 per cent. of moisture, and the greater part of the acid sodium sulphate has crystallised out. To test a benzol for thiophene, two or three drops of this reagent are put into a test tube, and 1 c.c. of benzol poured on to the top, and shaken up. The acid, as it creeps up the side of the test tube, at first becomes brown only, but in the presence of thiophene it presently becomes green, and finally a beautiful blue. If a very large quantity of thiophene be present, the reaction is instantaneous; with 2 to 3 per cent. it takes some minutes, and with very small quantities about a quarter of an hour. According to Schwalbe,<sup>6</sup> the reaction fails in the case of many coke-oven benzols; but Liebermann and Pens obtained the reaction in such products after allowing the test to stand for about three hours. In such extreme cases the reaction may be made more delicate by decanting off the benzol after the lapse of this time, and adding to the sulphuric acid remaining in the test tube several times its volume of pure concentrated sulphuric acid; a blue solution is then usually obtained.

In order to estimate the quantity of thiophene in commercial benzol, Denigès<sup>7</sup> recommends the use of a solution of mercuric sulphate

<sup>1</sup> *J. Soc. Chem. Ind.*, 1901, 20, 440.

<sup>4</sup> *Ibid.*, 1904, 37, 2461.

<sup>2</sup> *Ber.*, 1904, 37, 1244, 3128.

<sup>5</sup> *Ibid.*, 1887, 20, 3231.

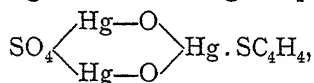
<sup>3</sup> *Ibid.*, 1904, 37, 1961.

<sup>6</sup> *Ibid.*, 1904, 37, 324.

<sup>7</sup> *Comptes rend.*, 1895, 120, 628, 781.

containing free sulphuric acid. This yields with thiophene a precipitate,  $(\text{HgSO}_4 \cdot \text{HgO})_2 + \text{C}_4\text{H}_4\text{S} + \text{H}_2\text{O}$ , insoluble in water and other ordinary solvents, from which thiophene is again liberated on warming with dilute hydrochloric acid or hydrogen sulphide. The test is carried out as follows:—Twenty c.c. of the mercury solution (prepared from 50 g. of mercuric oxide, 200 c.c. of concentrated sulphuric acid, and 1 litre of water) are added to 2 c.c. of the benzol, contained in a 60 c.c. flask provided with an air-tight stopper, and the mixture is warmed, with occasional shaking, for a quarter of an hour in a boiling water-bath. After cooling, the precipitate is filtered off on a tared filter, washed with hot water, and dried at  $110^\circ$  to  $115^\circ$ . The weight of thiophene is found by multiplying the weight of the precipitate by 0.0758. The mercury solution may also be treated with three times its volume of methyl alcohol, free from acetone, before adding the benzol. In this way complete solution of the benzol is obtained, and the precipitation is effected without warming, and very quickly; but it should be observed that in this case the mercury salt must be present in large excess, or otherwise a compound having the composition  $\text{SO}_4(\text{HgO})_2 \cdot \text{Hg} \cdot \text{C}_4\text{H}_4\text{S}$  is formed.

The latter compound also may, under suitable conditions, be used for the determination of thiophene, as in the following volumetric method of Denigès.<sup>1</sup> This is conducted as follows:—Two c.c. of benzol are mixed with 30 c.c. of methyl alcohol, free from acetone, and quickly treated with 10 c.c. of a solution prepared from 50 g. of red mercuric oxide dissolved in 200 c.c. of sulphuric acid and 1000 c.c. of water, vigorously shaken up, and allowed to stand for twenty-four hours. After filtering off the resulting compound,



21 c.c. of the filtrate, corresponding to 1 c.c. of benzol, are mixed in a litre flask with 350 c.c. of water, 15 c.c. of ammonia solution, 10 c.c. of *N*/10 potassium cyanide solution (standardised with *N*/10 silver nitrate solution), and five to six drops of a 20 per cent. solution of potassium iodide. After clearing the liquid, if necessary, by warming, it is titrated with *N*/10 silver nitrate solution till a permanent turbidity results. If *n* is the number of cubic centimetres of *N*/10 silver nitrate solution required, then the quantity of thiophene contained in 1 litre of benzol is  $(n - 0.3) \times 2.8$  g.

Subsequently Dimroth<sup>2</sup> found that thiophene combines with mercuric acetate, and stated that the reaction is suitable for its quantitative estimation. Schwalbe<sup>3</sup> examined both these methods of estima-

<sup>1</sup> *Bull. Soc. Chim.*, 1896, 15 [3], 1064; *Ber.*, 1896, 29, 1170.

<sup>2</sup> *Ber.*, 1902, 35, 2035.

<sup>3</sup> *Chem. Zeit.*, 1905, 29, 895.

tion by means of mercury compounds, and found that even absolutely thiophene-free benzene gives precipitates with mercuric salts, and, therefore, regards both methods as inaccurate. He then studied the qualitative indophenine reaction, and worked it out as a quantitative colorimetric method. Differences of 0.02 per cent. of thiophene can be easily recognised, 0.05 per cent. being the minimum and 0.5 per cent. the maximum quantity for which the method is available. The percentage of thiophene in pure and in commercial benzene is within these limits.

To carry out the test a number of standard solutions are required, which are prepared from benzene free from thiophene, and from absolutely pure thiophene. The following concentrations are adequate:—0.5, 0.25, 0.1, 0.075, 0.05, 0.025 and 0.01 per cent. A solution of 0.5 g. of isatin in 1000 g. of pure, concentrated sulphuric acid is also prepared; this solution will keep for months. Two portions, each of 25 c.c., of the isatin sulphuric acid reagent are introduced into two 100 c.c. flasks by means of a pipette, 25 c.c. of pure, concentrated sulphuric acid added to each, and then to one of them, 1 c.c. of the benzene-thiophene test solution, and to the other, 1 c.c. of the benzene to be tested. The flasks are stoppered, shaken well for five minutes, allowed to settle, and the resulting colorations compared against a white background. If the percentage of thiophene is not below 0.05 per cent., the first coloration is in all cases olive-green to bluish green. The smaller the content of thiophene, the more gradual is the appearance of the coloration, and the more green the shade of colour. An interval of fifteen minutes is sufficient for the comparison of the results. If a commercial benzene is to be tested, a commencement is made with the 0.5 per cent. test solution, and then with the more dilute test solutions in turn. In the case of pure benzenes, it is sufficient to test downwards from 0.25 per cent. or from 0.1 per cent. It is somewhat remarkable that the test, if carried out in a stoppered flask as described above, gives absolutely no recognisable green coloration when the thiophene content is 0.025 per cent., but only a faint grey discoloration of the yellow solution of the isatin reagent. If, however, the reaction is carried out in a porcelain basin, a green coloration, soon followed by blue, is obtained without difficulty with this proportion of thiophene. By employing a basin and comparing with test solutions of 0.025 and 0.01 per cent. of thiophene, very small proportions of thiophene can be estimated.

### 3. Paraffin Hydrocarbons (and Naphthenes).

The nitration method, formerly usual for the determination of the paraffins,<sup>1</sup> has since been abandoned on account of its inherent errors. The paraffins are now determined by converting the benzene hydro-

<sup>1</sup> Cf. Lunge, *Coal Tar and Ammonia*, p. 765.

carbons into soluble sulphonic acids. All substances which are neither destroyed nor sulphonated by fuming sulphuric acid remain in the residue, which, therefore, also includes the naphthenes and carbon bisulphide; the latter is determined by the method described above and its amount deducted.

According to Kraemer and Spilker,<sup>1</sup> this estimation is carried out as follows:—Two hundred grams of the sample are treated in a capacious separating funnel with 500 g. of fuming sulphuric acid containing 20 per cent. of anhydride, and shaken for a quarter of an hour, avoiding undue heating; the whole is then allowed to stand for two hours. The layer of sulphuric acid is drawn off, and the operation repeated twice with the same quantities of fuming acid. After treatment with 1500 g. of acid as above, everything except the paraffins, carbon bisulphide, and naphthenes has usually dissolved. The oil remaining in the funnel is collected, and the whole of the acid used is poured, with shaking, upon an equal weight of chopped ice contained in a 3 litre flask, taking care that the temperature does not rise above 40°. The solution is then boiled over a naked flame, and the free hydrocarbons present are distilled off and collected in a 100 c.c. separating funnel, the distillation being continued until 50 c.c. of water have passed over after the oil. In this manner all the oil dissolved by the sulphonic acids or mechanically mixed with the liquid is recovered and, after the water has been drawn off, is added to the main quantity. The whole of the oil is then again repeatedly shaken with 30 g. of fuming sulphuric acid containing 20 per cent. of SO<sub>3</sub>, until no further reduction in volume takes place, after which it is finally washed with a small quantity of water. The weight of oil obtained, divided by 2, gives the percentage of paraffins in the sample. This is scarcely more than 1 per cent. in the case of 90 per cent., 50 per cent., and 0 per cent. benzols; toluol usually contains none; xylol, on the contrary, often contains up to 3 per cent. of paraffins.

#### 4. Resinifiable Compounds (Cumarone, Indene, etc.), and Unsaturated Compounds (Hydrocarbons of the Ethylene and Acetylene Series).

J. Kent Smith<sup>2</sup> has proposed a colorimetric method for judging of the amount of impurities removed on shaking up a sample with sulphuric acid, which depends upon a comparison of the depth of coloration with certain brown, inorganic solutions of different concentrations. This process does not allow of any conclusion as to the quantity of non-nitratable substances.

Kraemer and Spilker state that the following similar colorimetric

<sup>1</sup> Muspratt, *Handbuch der technischen Chemie*, 4th ed., vol. 8, p. 43.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1899, 18, 212.

method is often used for testing the behaviour of commercial benzols with concentrated sulphuric acid:—Five c.c. of concentrated sulphuric acid are placed in a 15 c.c. stoppered bottle together with 5 c.c. of the sample, vigorously shaken for five minutes, and after being allowed to stand for two minutes the liquid is compared with 5 c.c. of a solution of potassium bichromate in pure 50 per cent. sulphuric acid, which is placed in a similar bottle, and covered with 5 c.c. of the purest benzene. Commercial benzols of 50 per cent. and 90 per cent. qualities should show by this test the colour of a solution of from 0.5 to at most 2.5 g. of bichromate per litre of 50 per cent. sulphuric acid. Xylene should show the same colour as a solution of from 1.0 to 2.0 g. bichromate per litre of acid; commercial, pure benzene and toluene should, on the contrary, not discolour the acid at all. The colour of the standard solutions will last for some time, but the pure benzene must be added separately every time a comparison is made.

In aniline colour works a commonly used method of estimating the loss on purification of commercial benzols when treated with sulphuric acid, is to shake 1000 g. of the benzol or toluol vigorously in a capacious separating funnel, for half an hour, together with 125 g. of sulphuric acid of sp. gr. 1.842, and then allow the mixture to stand. After the two layers have separated the acid is drawn off carefully, and the benzol washed several times in succession with 200 c.c. of water, and finally with dilute sodium hydroxide solution of a maximum strength of sp. gr. 1.04 to 1.07. Usually this treatment suffices, and it is only in the case of very bad benzols that it has to be repeated a second or even a third time, in which event only 50 g. of sulphuric acid are used for the last treatment. The need for further washing is ascertained by means of the test with bromine water (cf. *infra*), the benzol used for the test being again added to the main portion. The washed benzol is then dried with a few pieces of fused calcium chloride, and weighed. The loss in weight represents the loss on purification.

A measure of the quantity of unsaturated compounds (hydrocarbons of the ethylene and acetylene series, etc.) present in a crude benzol is afforded by titration with bromine. The bromine water formerly used for this purpose is best replaced by a solution of potassium bromide and bromate, which on addition of sulphuric acid, sets free 8.0 g. of bromine per litre. The test is carried out by Frank in the following manner:—Five c.c. of the sample are added to 10 c.c. of dilute sulphuric acid (1:5), contained in a 50 c.c. bottle provided with a glass stopper, and  $N/10$  bromide-bromate solution, containing 9.9167 g.  $KBr + 2.7833$  g.  $KBrO_3$  per litre, is added from a burette until, after five minutes shaking, bromine still remains. The titration is finished when the floating oil remains orange-red in colour after standing for fifteen minutes, and when one drop gives a dark blue coloration



with freshly prepared potassium iodide-starch paper. The quantity of bromine used (1 c.c. = 0.008 g. Br) should be given as such. To obtain accurate results, a preliminary determination is first made, and then two exact estimations, the mean of which is taken. Pure benzene and pure toluene should show a marked bromine reaction after the addition of 0.1 c.c. of the bromine solution, whilst 90 and 50 per cent. benzols will decolorise, on an average, 0.6 c.c. of the reagent, but seldom more than 1 c.c. Commercial xylene absorbs 2 per cent. of bromine in a few minutes, and considerably more on standing for some time.

## II.—NAPHTHALENE

Naphthalene comes on the market in various grades, differing in appearance and quality according to the purpose for which it is to be used. Pressed or filtered crude naphthalene is used, as a raw material, in the manufacture of lamp black, also for preserving raw hides, and, more recently, for driving explosion motors. The pure, distilled product is employed in the form of cakes or in a powdered form in the aniline colour industry, sublimed naphthalene for fumigating purposes, and compressed into tablets, candles, or balls, it is used as a household disinfectant and for the disinfection of urinals, etc.

The examination of crude naphthalene has been described under the heading "Middle Oil" (p. 772).

The aniline dye industry requires a chemically pure naphthalene which volatilises without residue, melts at exactly  $79^{\circ}.6$  to  $79^{\circ}.8$ , and boils at  $217^{\circ}$  to  $218^{\circ}$ ; it must be as odourless as possible, and dissolve in petroleum benzine to a water-clear liquid which must be perfectly colourless. The monosulphonic acid produced by sulphonation must not show any grey tinge, and its sodium salt must be snow-white in colour. Naphthalene only fulfils these requirements when it does not turn yellow in colour on exposure to air and light, and when it shows a faint rose tint only when dissolved in perfectly clear, pure, concentrated sulphuric acid. In order to test the stability of its colour on exposure to air and light, the naphthalene is placed on a watch-glass over pure, concentrated, non-fuming nitric acid, the whole being covered with a bell-jar. Under these conditions it should remain colourless for at least one to two hours; after several hours even the purest naphthalene becomes yellowish on the surface owing to the formation of nitro-compounds. If not thoroughly purified, naphthalene contains slight traces of phenols which are detected by extracting with sodium hydroxide, acidifying the solution with hydrochloric acid, and adding bromine water, when tribromphenols are formed (*cf.* Examination of carbolic acid). Basic compounds are seldom found in naphthalene; they can be detected by their characteristic smell after extracting with

concentrated sulphuric acid, adding sodium hydroxide in excess to the filtrate, and distilling in a current of steam.

The temperature of solidification has been adopted, by agreement, as the melting point of pure naphthalene, and is determined by Shukoff's method.<sup>1</sup> The method is very accurate, and the results obtained by different observers hardly differ by  $\frac{1}{10}^{\circ}$ . Shukoff's apparatus consists of a double-walled vacuum jacketed glass vessel, inside which a thermometer graduated in  $\frac{1}{10}^{\circ}$  is suspended by means of a bored cork. The vessel is filled with melted naphthalene, which is heated a few degrees above its melting point, and the thermometer placed in position, when it is at once covered with a layer of solid naphthalene. The thermometer rises, and finally shows the temperature of the fused naphthalene. After waiting until the thermometer indicates about  $3^{\circ}$  above the approximate melting point, the vessel is shaken until its contents are turbid. The vessel is then allowed to stand, while the thermometer is continually observed until the temperature remains constant. The true melting or solidifying point is the temperature at which the mercury thread remains stationary for at least five minutes.

A. H. White and S. Ball<sup>2</sup> estimate naphthalene in tar by weighing about 1 g. of tar into a 50 c.c. Erlenmeyer flask which is provided with a double bored cork, one perforation serving as an air inlet while the other carries a U-tube. The first two-thirds of this tube is filled with quicklime and the remaining space with glass wool and phosphorus pentoxide. The entire apparatus is contained in an air-bath at a temperature of  $70^{\circ}$  to  $80^{\circ}$ . The outlet of the U-tube is connected, outside the air-bath, by means of a short piece of rubber tubing, with a weighed, second U-tube immersed in ice water. A current of air is drawn through the apparatus by an aspirator at a velocity of 2 litres per hour, which causes the naphthalene to volatilise and to deposit in the cooled U-tube. The operation is continued until the second U-tube no longer shows an increase in weight. The method is stated to be sufficiently accurate for ordinary purposes, although the naphthalene deposited is not quite pure.

Naphthalene can almost always be detected in technical products by its great volatility at low temperatures, and by its characteristic smell. Vohl has suggested a test depending on the red coloration which its nitro-compound, obtained by the action of fuming nitric acid, yields when boiled with alkali-sulphides; this test is, however, not reliable.

According to Küster,<sup>3</sup> naphthalene can be quantitatively estimated in the form of its picric acid compound,  $C_{10}H_8 + C_6H_2(NO_2)_3OH$ . The

<sup>1</sup> *Chem. Zeit.*, 1901, 25, 1111.

<sup>2</sup> *J. Gas Lighting*, 1904, 88, 262 and 323.

<sup>3</sup> *Ber.*, 1894, 27, 1101.

determination can be carried out volumetrically by using an excess of aqueous picric acid solution and titrating back. Other substances which form picrates, such, for instance, as a number of the aromatic hydrocarbons, must, of course, be absent.

A method for the detection of colophonium in naphthalene has been described by Hodurek.<sup>1</sup>

### III.—ANTHRACENE

Anthracene is never met with commercially as a pure compound but only as a crude product of varying degrees of purity. A distinction is made between an "A" and a "B" quality. The former is usually of higher percentage and contains less paraffin and methyl anthracene than the "B" quality, which latter is mainly derived from gas tar partially produced from cannel coal and other coals, which yield products of the paraffin series.

Zeidler<sup>2</sup> and others who have investigated crude commercial anthracene have isolated the following substances:—Acenaphthene, fluorene, phenanthrene, carbazol, anthracene, acridine, fluoranthene, pseudo-phenanthrene, pyrene, methylanthracene, chrysene, parachrysene, (picene?), phenylnaphthylcarbazol (chrysogene?); naphthalene and solid paraffins are also present.

The technical analysis of crude anthracene only deals with the content of pure anthracene and with the presence of injurious impurities such as methylanthracene, paraffin, etc.

#### (a) Sampling.

The sampling should be carefully performed under the general conditions described in Vol. I., pp. 7-17. The barrels containing anthracene are bored at each end and often on two sides, and a sample taken from each hole with a Gawalowski or Angerstein auger (Vol. I., p. 13); the united samples are then well mixed in a large mortar and passed through a sieve. Three samples are taken from this mixture and sealed, one for the buyer, one for the vendor, and a third as a control in case of dispute.

#### (b) Analysis.

The anthracene in technical products is exclusively determined as anthraquinone according to the method worked out by E. Luck<sup>3</sup> in the laboratory of the Farbwerke vorm. Meister Lucius und Brüning. Earlier methods of analysis are the alcohol method, Perkins petroleum, and carbon bisulphide method, Cohn's carbon bisulphide

<sup>1</sup> *Oester. Chem. Zeit.*, 1902, p. 555.

<sup>2</sup> *Annalen*, 1878, 191, 285.

<sup>3</sup> *Z. anal. Chem.*, 1877, 16, 81.

method, and various modifications of the latter. The decisive comparisons conducted by F. H. Davis and Lucas showed that all these methods are valueless for technical purposes.

Luck's method, which is also termed the "Höchst Anthracene test," is conducted as follows:—One gram of the sample is weighed into a 500 c.c. flask, 45 c.c. of glacial acetic acid is added, and the flask connected by means of a good cork to a condensing tube about 75 cm. long. To the upper end of this is fixed, by means of two rubber rings, a test tube of about 50 c.c. capacity which contains a solution of 15 g. of chromic acid crystals dissolved in 10 c.c. of glacial acetic acid and 10 c.c. of water. The contents of the flask are heated over a sand-bath till they boil gently. The chromic acid solution is then allowed to flow through a small capillary syphon into the boiling contents of the flask at such a rate that it is all just added in two hours. A small dropping-funnel may be used instead of the syphon, but the latter is safer and needs no subsequent regulation when once adjusted. After all the chromic acid solution has been added, the contents of the flask are allowed to boil for another two hours, taking care that no vapour escapes from the condenser. After standing for twelve hours, 400 c.c. of water are added, which causes the anthraquinone to separate completely. This is filtered off, washed with cold, distilled water, then with weakly alkaline, boiling water, till the filtrate remains clear on acidifying, and finally with pure, boiling water until the filtrate is no longer alkaline. The filter is then carefully removed from the funnel, spread out upon a clean glass plate, and its contents rinsed into a small, flat, tared, porcelain dish, and dried at  $100^{\circ}$  until the weight remains constant; the weight of crude anthraquinone is thus found. Ten grams of slightly fuming sulphuric acid are now added to the anthraquinone in the dish, heated for ten minutes on an air-bath to  $112^{\circ}$ , then allowed to stand in a damp place for twelve hours to absorb water, and rinsed into a 300-400 c.c. basin with 200 c.c. of water. After cooling, the precipitate is filtered off, washed as above with cold water, boiling, weakly alkaline water, and lastly with plain hot water, rinsed into a small porcelain dish and dried at  $100^{\circ}$  to constant weight. The dish is then heated over a sand-bath until all the anthraquinone has volatilised, allowed to cool in a desiccator, and again weighed. The difference between these two last weighings gives the weight of pure anthraquinone, which, when multiplied by 0.8558, gives the weight of anthracene. A correction for the anthraquinone<sup>1</sup> remaining in solution in the glacial acetic acid is not required, as this error is compensated by others resulting from the methylanthracene and paraffin in the crude anthracene, and the resulting presence of anthracene carboxylic acid in the final product.

<sup>1</sup> Holland, printed circular, dated Manchester, February 1879.

The following table of equivalent weights of anthraquinone and anthracene has been drawn up by Lunge :—

Anthraquinone.	Anthracene.	Anthraquinone.	Anthracene.	Anthraquinone.	Anthracene.
1	0.86	35	29.95	68	58.21
2	1.71	36	30.81	69	59.06
3	2.56	37	31.66	70	59.91
4	3.42	38	32.53	71	60.77
5	4.28	39	33.38	72	61.62
6	5.14	40	34.23	73	62.47
7	5.99	41	35.09	74	63.33
8	6.86	42	35.94	75	64.19
9	7.71	43	36.79	76	65.05
10	8.56	44	37.65	77	65.90
11	9.42	45	38.51	78	66.77
12	10.27	46	39.37	79	67.62
13	11.16	47	40.22	80	68.46
14	11.98	48	41.09	81	69.32
15	12.84	49	41.94	82	70.17
16	13.70	50	42.79	83	71.02
17	14.55	51	43.65	84	71.88
18	15.42	52	44.50	85	72.74
19	16.27	53	45.35	86	73.60
20	17.12	54	46.21	87	74.45
21	17.98	55	47.07	88	75.32
22	18.83	56	47.93	89	76.17
23	19.68	57	48.78	90	77.02
24	20.54	58	49.65	91	77.88
25	21.40	59	50.50	92	78.73
26	22.26	60	51.35	93	79.58
27	23.11	61	52.21	94	80.44
28	23.98	62	53.06	95	81.30
29	24.83	63	53.91	96	82.16
30	25.67	64	54.77	97	83.01
31	26.53	65	55.63	98	83.87
32	27.38	66	56.49	99	84.73
33	28.23	67	57.34	100	85.58
34	29.09				

According to Basset,<sup>1</sup> the anthraquinone produced as above contains certain impurities, causing the results of the analysis to be slightly too high. To remove these impurities he proposes to boil the anthraquinone with chromic acid solution and nitric acid, whereby there is a loss of 1 to 2 per cent., leaving chemically pure anthraquinone. He subsequently found<sup>2</sup> that the result of the analysis is influenced by the purity of the glacial acetic acid used. A sample of acetic acid melting at 16°.7 itself reduced 0.16 g. of chromic acid out of 15 g. in twenty-four days in the cold, whilst another sample melting at 13°.3 reduced 0.87 g. After boiling for four hours under the conditions observed during anthracene determination, the purer quality reduced 4.44 out of 15 g. of chromic acid, and the more impure quality 6.45 g. The results of these experiments point to the following sources of error:—If acetic acid of inferior quality be used the results will be

<sup>1</sup> *Chem. News*, 1896, 73, 178.

<sup>2</sup> *Ibid.*, 1899, 79, 157.

too high, and if the stock of chromic acid solution be kept too long it will lose strength by reduction, leading to a similar error in the final result of the analysis. In this connection it may be noted that commercial glacial acetic acid usually contains small quantities of glyoxylic acid.

C. Nicol<sup>1</sup> determines the anthracene in coal tar directly as follows:—Twenty grams of the tar are distilled from a retort and the vapours passed into a U-tube, which is heated to 200° in a paraffin bath. By this means all ingredients of low boiling point are volatilised whilst the anthracene and its accompanying impurities remain in the U-tube. As a part of the anthracene remains in the neck of the retort, this is cut off, powdered, and added to the contents of the U-tube. These are then dissolved in glacial acetic acid, and the anthracene determined by Luck's method. This procedure, however, never gives reliable results, as it is not possible to stop the distillation exactly as is done on a large scale, and thus to avoid decomposition of the pitch.

### (c) Detection and Estimation of the Impurities present in Commercial Anthracenes.

*Methylantracene* is an objectionable impurity of crude anthracene, as it exercises a bad effect upon the shade of the alizarin produced; anthracene which has been distilled from cannel coal tar or from coal tar pitch is especially liable to contain this impurity. When present, the anthraquinone obtained on analysis does not show the usual characteristic needles, but appears in a more felted condition. Schultz and Japp,<sup>2</sup> who were the first to discover methylantracene in crude anthracene, described a method for its separation, which depends upon the previous oxidation of the anthracene by bichromate and sulphuric acid, and the subsequent distillation of the residue and treatment of the distillate with alcohol. Phenanthrene first crystallises out from the alcoholic solution, and the methylantracene can be obtained from the mother liquor. According to A. G. Perkin,<sup>3</sup> the best method of determining the value of an anthracene containing methylantracene, in doubtful cases, is its conversion into alizarin.

*Phenanthrene* is an important constituent of crude anthracene. Kraemer and Spilker give the following method for its estimation, which, however, only gives satisfactory results when it is present in large quantity:—One kilogram of crude anthracene is dissolved in 2 kilos of toluene, and allowed to crystallise for about six hours at the ordinary temperature, with frequent stirring. The anthracene and carbazol, which crystallise out, are separated by filtration on the pump

<sup>1</sup> *Z. anal. Chem.*, 1876, 15, 318.

<sup>2</sup> *Ber.*, 1877, 10, 1049.

<sup>3</sup> *J. Soc. Dyers and Col.*, 1897, p. 81; *J. Soc. Chem. Ind.*, 1897, 16, 563.

and washed with 200 c.c. of toluene. After removing the toluene from the combined filtrate and washings by distillation, the residue is fractionally distilled, the portion distilling over between  $280^{\circ}$  and  $340^{\circ}$  being crude phenanthrene. This is used for the estimation as follows:—Twenty grams are boiled for half an hour with 30 g. of picric acid in 300 c.c. of dry xylene in a flask with a reflux condenser. After standing for twenty-four hours with frequent shaking, the crude phenanthrene picrate is filtered on the pump, dried, and weighed. The mother liquor is diluted with 50 c.c. of xylene, and a further 20 g. of crude phenanthrene together with 30 g. of picric acid dissolved in it. The difference between the quantity of crude picrate now obtained and that of the first crystallisation gives the amount dissolved in 250 c.c. of cold xylene. From the solubility so obtained, and the weight of the two crystallisations, the united amount of crude picrate derived from 40 g. of crude phenanthrene is ascertained. An aliquot part of this is now crystallised from 95 per cent. alcohol. The pure picrate, which forms brilliant yellowish red needles, is weighed and to its weight is added an allowance for that remaining in solution in the alcohol (20 g. in 750 g. of 95 per cent. alcohol). One hundred parts of pure picrate correspond to 43.7 parts of pure phenanthrene. If the phenanthrene be very impure, 30 g. of the sample and 45 g. of picric acid are used each time. The quantity of xylene added after the first crystallisation is, in this case, increased from 50 to 200 c.c. The difference in weight of the two crystallisations then represents the solubility of the crude picrate in 100 c.c. of xylene. The picrate which is obtained is tested for purity by decomposing it with ammonia and weighing the hydrocarbon, after removing any acridine which may be present by washing with dilute sulphuric acid.

According to H. Behrens,<sup>1</sup> phenanthrene is easily detected in crude anthracene by extracting with benzene, evaporating the extract, and treating the latter with a solution of  $\alpha$ -dinitrophenanthraquinone in nitrobenzene.

*Carbazol and Phenyl-naphthylcarbazol.*—These substances exercise, like methylanthracene, an unfavourable influence on the purification of the anthraquinone. According to H. Behrens,<sup>2</sup> carbazol is easily detected by extracting with ethyl acetate in the cold, evaporating the solvent on a watch-glass, and warming with a few drops of nitrobenzene and phenanthraquinone; characteristic, narrow plates of a coppery lustre are thus obtained.

Carbazol, which has risen in importance commercially, especially as a raw material for the manufacture of potassium cyanide and ferrocyanide,<sup>3</sup> is usually determined quantitatively, according to Kraemer

<sup>1</sup> *Rec. trav. Chim.*, 1902, 21, 252; *J. Soc. Chem. Ind.*, 1902, 21, 1250.

<sup>2</sup> *Rec. trav. Chim.*, 1902, 21, 252; *Chem. Centr.*, 1902, 11, 540.

<sup>3</sup> Ger. Pat. 81237.

and Spilker, by either of the two following methods. In the first of these the bases are previously extracted from the sample with warm, dilute sulphuric acid, and the nitrogen determined in the residue by Kjeldahl's method; from this the amount of carbazol is calculated. The second method depends on the fact, observed by Kraemer and Spilker, that carbazol is converted into its potassium derivative by the action of potassium hydroxide at  $220^{\circ}$  to  $240^{\circ}$ . The estimation is carried out as follows:—Forty grams of 80 to 85 per cent. potassium hydroxide are melted in a steel crucible of 80 c.c. capacity of the form shown in Fig. 132, the thick wall of which contains a cavity for the reception of a thermometer. The temperature is then kept at  $180^{\circ}$  to  $200^{\circ}$  whilst 20 g. of the crude carbazol or crude anthracene are stirred in. The lid is then placed on the crucible, the temperature kept at  $220^{\circ}$  to  $230^{\circ}$  for an hour, with frequent shaking, the lid removed, any sublimate returned to the crucible, and the anthracene and other associated compounds driven off at a temperature not exceeding  $240^{\circ}$ . Two hours suffice for this purpose in the case of carbazol of a high degree of purity, and too much heating is to be avoided. After allowing to cool, the melt is ground up with hot water, made distinctly acid with dilute sulphuric acid, the carbazol collected on a filter, washed, dried, and weighed. The product is usually dark coloured and must be purified with toluene, of which 600 to 800 c.c. should be used for carbazols of high percentage. The boiling toluene solution is passed through a folded filter which is afterwards washed with a small, measured quantity of toluene. The solution is usually brown, and on standing at  $14^{\circ}$  to  $18^{\circ}$  for twelve hours deposits a portion of the carbazol in crystals, which are filtered off on the pump, dried, and weighed. The filtrate is measured at  $17^{\circ}$  and the amount of carbazol in solution calculated according to the solubility table prepared by Becchis,<sup>1</sup> as 0.48g. per 100 c.c. A further allowance for loss of 0.5 g. must be added to the final weight of carbazol obtained. This method does not give very reliable results.

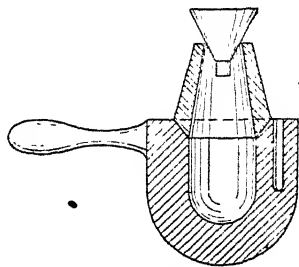


FIG. 132.

W. Vaubel<sup>2</sup> determines carbazol volumetrically by dissolving it in glacial acetic acid, and adding a standardised potassium bromate solution containing potassium bromide, until a bromine reaction persists for some time. Each molecule of carbazol absorbs 2 mols. of bromine, although only a monobromo-derivative is formed, in consequence of the oxidation of the imido-group.

<sup>1</sup> *Jahresber.*, 1879, p. 376.

<sup>2</sup> *Z. angew. Chem.*, 1891, 4, 748.



Nickels<sup>1</sup> detects phenylnaphthylcarbazol spectroscopically in the benzene solution of crude anthracene by means of two well-defined black bands between lines F and G, and a third which is still more refractive than G.

*Paraffins.*—Allen<sup>2</sup> adopts the following method for the estimation of the paraffins in crude anthracene:—Ten grams of the sample are heated on the water-bath with 200 g. of strong sulphuric acid, till all is dissolved except a portion of the paraffin which separates as oily drops on the surface. The solution is poured into 500 c.c. of water and allowed to cool: the paraffin rises to the surface and solidifies to a film, which can be lifted out, dried between filter paper, and weighed.

If only small quantities of paraffin are present, the separated paraffin is extracted by shaking twice successively with ligroin, the extract washed with half its volume of 5 per cent. sodium hydroxide solution, then four times with one-fourth of its volume of concentrated sulphuric acid, and finally with water. The ligroin is then distilled off, in a weighed flask, on the water-bath, and the residual paraffin weighed.<sup>3</sup>

F. Heusler and E. Herde<sup>4</sup> add 25 c.c. of fuming nitric acid, drop by drop, to 2 g. of crude anthracene in a 150 c.c. flask, cooling meanwhile with ice water. The whole is allowed to stand until the anthracene has completely dissolved, warmed for a short time on the water-bath to allow the paraffin to collect into drops, then cooled, and the acid liquid filtered on the pump through a small asbestos filter. The paraffin which remains on the filter is washed with fuming nitric acid until the washings no longer become turbid on dilution, then washed with water until free from acid, rinsed with warm alcohol into a small, tared porcelain dish, and the filter washed into a test tube with ether. The alcohol is then evaporated on the water-bath, the ethereal liquid added, and the ether allowed to evaporate at the ordinary temperature. The paraffin which remains is dried at 105° to 110°, and weighed.

Kraemer and Spilker<sup>5</sup> recommend the following procedure:—Ten grams of the very finely ground anthracene are shaken for some time with 70 c.c. of ether in a 100 c.c. measuring flask, which is then filled up to the 100 c.c. mark with ether, mixed well, and allowed to stand till the solid has settled to the bottom. Fifty c.c. of the clear liquid are then transferred by means of a pipette into a porcelain dish, the ether evaporated, and the residue dried for half an hour at 100°. When cold, the residue is powdered as finely as possible in the dish, well mixed with 8 c.c. of fuming sulphuric acid (20 per cent. of

<sup>1</sup> *Chem. News*, 1874, 40, 270; 1875, 41, 52, 95, 117.

<sup>2</sup> *Commercial Organic Analysis*, vol. 2, p. 259.

<sup>3</sup> *Cf. Oil and Colour J.*, 1906, p. 487.

<sup>4</sup> *Z. angew. Chem.*, 1895, 8, 253.

<sup>5</sup> Muspratt, *Handbuch der technischen Chemie*, 4th ed., vol. 8, p. 70.

$\text{SO}_3$ ), and heated to  $100^\circ$  for three hours, covering the dish with a watch-glass meanwhile and stirring frequently. The contents of the dish are then rinsed into a beaker with 500 c.c. of hot water, filtered when cold through a moist filter, and washed with cold water until barium chloride causes no precipitate with the washings. The filter is well drained and rinsed with a little alcohol, after which the paraffin is dissolved out with ether into a weighed porcelain dish. Any traces of paraffin still remaining in the beaker are also washed into the dish with ether. The ethereal solution is evaporated at a gentle heat, dried for half an hour at  $105^\circ$ , and weighed as paraffin.

*Hydrocarbons.*—The hydrocarbons of coal tar, and hydrocarbons in general, can be quickly identified by the method of E. Lippmann and J. Pollak,<sup>1</sup> who make use of the colorations which their solutions in strong sulphuric acid yield on addition of benzal chloride,  $\text{C}_6\text{H}_5\cdot\text{CHCl}_2$ , in the cold. These are as follows:—

Anthracene	.	.	Malachite green.
Naphthalene	.	.	Magenta red.
*Benzene	.	.	Light yellow.
*Toluene	.	.	Light yellow.
*Xylene	.	.	Orange.
Phenanthrene	.	.	Carmine.
Triphenylmethane	.	.	Pale yellow.
Picene	.	.	Olive green, after some time.
Diphenylmethane	.	.	Brick red.
Stilbene	.	.	Bluish green.
*Pseudocumene	.	.	Orange red.
*Cymene	.	.	Orange.
Pyrene	.	.	Emerald green, later deep blue.
Acenaphthene	.	.	Dark blue.
Dibenzylanthracene	.	.	Yellowish green.
Chrysene	.	.	{ Light yellow, then light green ; later dark green.

The hydrocarbons marked \* yield the coloration mentioned even without addition of benzal chloride.

#### IV.—CARBOLIC ACID, CRESOLS, AND CARBOLIC ACID PREPARATIONS

The term "carbolic acid" as used in the chemical trade, is by no means well defined or limited to a definite chemical compound. It not only denotes the pure phenol,  $\text{C}_6\text{H}_5\text{OH}$ , but also the cresols, their mixtures with phenol, and further the crude tar oils containing only a certain percentage of these substances in the crudest state. In this section phenol will first be considered, then the cresols, and finally carbolic acid preparations, including crude tar oils and manufactured preparations containing phenol and cresols. The analytical

<sup>1</sup> *Monatsh.*, 1902, 23, 670.

methods which have been proposed for these substances are very numerous, but only those will be discussed which are of importance from a technical standpoint, and are used in that connection. For further information reference may be made to G. Lunge's *Coal Tar and Ammonia*, 4th edition, 1909, and to H. Kohler's *Karbolsäure und Karbolsäurepräparate*.

The following are the chief commercial products.

#### (a) Crude Phenol.

This is chiefly a product of the English market, and serves for the manufacture of crystallised carbolic acid and of cresols. In the cold it solidifies to a crystalline magma. If 50 per cent. is distilled and the distillate cooled to 15°, crystals of phenol are obtained, and in this way the product is easily distinguished from crude cresol (100 per cent. crude carbolic acid). As a rule, the analysis is limited to the estimation of the percentage of water, the solidifying point, and solubility, all of which are carried out in one operation by the method described under "Carbolic Oil," p. 773.

Water is completely separated from the first portion of the distillate by mixing this with three to four times its volume of benzene. The solubility is ascertained by thoroughly shaking one part of crude phenol with four parts of 10 per cent. potassium or sodium hydroxide solution; the resulting solution must be clear, and must not become turbid on dilution with water.

#### (b) Phenol (*Carbolic Acid Crystals*).

In the pure state, phenol forms a white, vitreous, translucent, crystalline mass, melting at 42° and boiling at 184°; it melts to a strongly refracting colourless liquid possessing a peculiarly harsh, but not unpleasant aromatic odour. The sp. gr. at 15° is 1.066; at the ordinary temperature it is soluble in about fifteen parts of water.

Products appear on the market with varying melting points (from 42°, 39° to 40°, and below to 32°) conditioned by the presence of small quantities of moisture and of cresols which strongly influence this property.

The most important application of phenol is in the manufacture of picric acid; considerable quantities are employed in the manufacture of salicylic acid and of aniline dyes, while its use in surgery (formerly the chief consumption) is continually diminishing, in consequence of the increased employment of the cresols, which are more strongly antiseptic but less corrosive.

Synthetic phenol made from benzene behaves, in all essential points, exactly as tar phenol.

The following determinations are to be considered in the analysis

of phenol:—The melting point, or, more correctly, the solidifying point, the test for clear solubility in 10 per cent. sodium hydroxide solution and in water, the colour, and the odour.

On account of its strong hygroscopic property, too low results by  $1^{\circ}$  to  $2^{\circ}$  are obtained if the melting point is determined in capillary tubes in the usual way, for which reason the estimation of the solidifying point is accepted as the standard determination. Kraemer and Spilker state that the following precautions are necessary for the determination of the solidifying point of a large sample of phenol. The sample is completely melted in an air-bath or drying-oven, from which moisture is completely excluded, it is then thoroughly mixed, and about 50 c.c. removed into a wide-mouthed flask, where it is continually stirred with a thermometer graduated in  $\frac{1}{10}^{\circ}$ . The flask and its contents are allowed to cool slowly, so that when in the neighbourhood of the solidifying point the temperature falls, at most, half a degree per minute. The temperature at which a crystal of pure phenol, when added to the contents, will grow, is the true solidifying point. If the flask has cooled below this point, there is a vigorous formation of crystals, accompanied by a rise of temperature, and the correct solidifying point is the highest temperature thus indicated. The apparatus recommended by Shukoff (p. 803) is the most suitable for the determination.

Complete solubility in sodium hydroxide solution is tested for as described above. The test is more exact if water is substituted for the alkaline solution; one part of phenol should give an absolutely clear solution with fifteen parts of water.

Phenol (also the synthetic compound) frequently shows a pink colour; a penetrating odour of sulphur compounds or of other tar products should not be noticeable. No further determinations are, as a rule, required for the valuation of commercial phenol.

### (c) Cresols (*Cresylic Acid*).

Coal tar cresol is a mixture, in varying proportions, of the three isomeric cresols, in which the *m*-cresol predominates.

Their boiling points are:—

<i>o</i> -Cresol	.	.	.	.	.	191°
<i>m</i> - "	.	.	.	.	.	203°
<i>p</i> - "	.	.	.	.	.	202°

Thus the differences in boiling point are so small that the separation of the isomers by distillation is only possible in the case of the *o*-cresol, which after repeated fractionation can eventually be obtained in a pure condition. In addition to the isomeric cresols, crude tar cresol usually contains some phenol, the boiling point of which is only  $7^{\circ}$  lower than that of *o*-cresol.

According to Ihle,<sup>1</sup> Tiemann and Schotten,<sup>2</sup> and K. E. Schulze<sup>3</sup> the proportions of the three isomers in coal tar cresol vary. The latter found:—

<i>m</i> -Cresol	.	.	.	.	About 40 per cent.
<i>o</i> - "	.	.	.	.	" 35 "
<i>p</i> - "	.	.	.	.	" 25 "

Their solubility in water at the ordinary temperature is, according to Gruber:—

Pure <i>o</i> -Cresol	.	.	.	.	2.50 volumes per cent.
" <i>m</i> - "	.	.	.	.	0.53 " "
" <i>p</i> - "	.	.	.	.	1.80 " "
Cresol mixture from toluidine	.	.	.	.	2.20 " "
" " tar oil	.	.	.	.	2.55 " "

On the other hand, the anhydrous cresol mixture from coal tar can take up 5 per cent. of water.<sup>4</sup>

The chief commercial products of cresol are:—

*Liquid Carbolic Acid, 100 per cent. (Dark).*—An almost black liquid which dissolves in sodium hydroxide either to a clear or turbid solution, and boils between 185° and 210°. It consists chiefly of a mixture of the three isomeric cresols, together with a considerable proportion of phenol, xylenols, and higher methylated phenols, and is used for crude disinfecting purposes, and for the preparation of the other commercial products.

*Liquid Carbolic Acid, 100 per cent. (Light).*—A yellow or brownish liquid which boils between somewhat narrower limits of temperature than the above and behaves similarly towards sodium hydroxide. It is used chiefly for pharmaceutical purposes.

*Purified Cresylic Acid or Tricresol.*—A colourless liquid of boiling point 185° to 205°, consisting essentially of the three isomeric cresols with traces only of phenol and of higher methylated homologues.

*Technical Meta-Cresol.*—A yellowish liquid which is usually made in two qualities, one of which is used in pharmacy; this has a boiling point of 199° to 204° and contains a small proportion of *o*-cresol, from 58 to 60 per cent. of *m*-cresol, the remainder being *p*-cresol.

The impurities found in cresol comprise phenol, water, and hydrocarbons. For most purposes phenol can hardly be considered as an impurity; its approximate amount can be determined as described below. The water is determined by distillation as in the case of phenol. J. Muter<sup>5</sup> tests for the presence of water by shaking the sample in a graduated tube with three times its volume of concentrated, saturated salt solution; if the cresol is free from water, its volume increases

<sup>1</sup> *J. prakt. Chem.*, 1876, **14**, 451.

<sup>2</sup> *Ber.*, 1878, **11**, 768.

<sup>3</sup> *Ibid.*, 1887, **20**, 410.

<sup>4</sup> Muter, *Chem. Centr.*, 1890, p. 840.

<sup>5</sup> *Ibid.*

under this treatment by about 5 per cent.; if saturated with water, its volume remains unchanged. Hydrocarbons, such as naphthalene are detected by removal of the cresol with dilute sodium hydroxide solution, as described in the case of phenol.

There are no characteristic reactions known for distinguishing cresols from phenol, as all reactions of the latter are shared by the former. The relatively more sparing solubility of cresols in water is the characteristic which lends itself most readily to analytical purposes. Allen<sup>1</sup> has given a tabular summary of the relative behaviour of cresol and phenol in this respect. The boiling point is also a reliable guide both as to the composition of the pure products and their mixtures.

The value of commercial cresol (cresylic acid) is dependent for some purposes on the proportion of *m*-cresol which is present. Various methods of determining the *m*-cresol in these mixtures have, therefore, been proposed, of which the following are in use for technical purposes. The method of F. Raschig<sup>2</sup> depends on the fact, that on treating *m*-cresol with excess of nitric acid at 100°, it is quantitatively converted into trinitrocresol, whilst its isomers are completely oxidised, forming oxalic acid. The following directions, which must be most carefully observed, give very reliable results. Exactly 10 g. of the cresol mixture are weighed into a small conical flask, mixed with 15 c.c. of ordinary sulphuric acid of sp. gr. 1.84, then heated for one hour in a steam oven, and the contents poured into a wide-necked flask of 1 litre capacity. The flask is cooled under the tap, shaking it round meanwhile in such a manner that the sulphonic acid, which is a mobile liquid, whilst hot, settles as a thick syrup on the sides of the flask during cooling. Ninety c.c. of nitric acid of sp. gr. 1.38 are then first poured into the small flask in which the sulphonation was conducted, in order to remove any sulphonic acid adhering to its sides, rinsed well round, and then poured, all at once, into the large flask. The contents of the latter are well shaken immediately, so that all the sulphonic acid is dissolved, which takes about twenty seconds, and the flask then placed in a draught-cupboard. After one minute a violent reaction occurs, red fumes are evolved, and the liquid boils; then it suddenly becomes turbid, oily drops of trinitrocresol form and collect on the bottom of the flask, and after five minutes the reaction is apparently ended. The whole is allowed to stand for at least another five minutes, then poured into a dish containing 40 c.c. of water, and the flask rinsed out with a further 40 c.c. of water into the same dish. On mixing with the water the trinitro-*m*-cresol solidifies, with liberation of nitrous fumes, to a crystalline magma. It is allowed to stand for at least two hours whilst the liquid cools, is then crushed with a pestle, and filtered on the pump through a filter which has been tared against

<sup>1</sup> Lunge, *Coal Tar and Ammonia*, p. 216.

<sup>2</sup> *Z. angew. Chem.*, 1900, 13, 759.

another one. The crystals of trinitrocresol are washed with 100 c.c. of water, dried at 95° to 100°, and weighed. If these instructions are carefully followed 1.74 g. of trinitro-*m*-cresol are obtained for each 1.0 g. of *m*-cresol present in the mixture, whatever the composition of the latter. The presence of even 10 per cent. of phenol does not diminish the accuracy, as the picric acid which is formed remains in solution; but the method must not be applied to mixtures containing very large amounts of phenol, which, however, do not often occur in practice. In such samples the presence of phenol is detected by the boiling point, and also by the fact that the nitro-compound does not remain solid in the steam-oven at 95° to 100°, but melts, or at any rate, forms a soft paste. Xylenols, which sometimes occur in commercial cresols, behave in a similar manner; the nitro-compound either liquefies when warm or refuses to set in the cold. But a cresol which distils for the most part between 190° and 200°, and, therefore, contains scarcely any phenol or xyleneol always yields a pale yellow crystalline mass, the weight of which when divided by 1.74 gives the weight of *m*-cresol in the mixture, the error being within 1 per cent. The amount of nitric acid used is considerably more than is needed for the nitration and oxidation, and good results can be obtained with average cresols containing 35 to 60 per cent. *m*-cresol, when only 70 c.c. of nitric acid are used; but if this is done the reaction often occurs so suddenly that there is scarcely time to mix the sulphonic acid with the nitric acid and place the flask on one side; explosions have even been known to occur under these conditions. The recognised quantity of 90 c.c. of acid is, therefore, adhered to, and is poured, all at once, into the flask as quickly as possible, a flask having a very wide neck being used.

F. Russig and G. Fortmann<sup>1</sup> have described a method which is used in France. This is not so simple or rapid as Raschig's method, but gives rather higher results, probably because the nitration is more complete; it is also inapplicable for mixtures containing more than 10 per cent. of phenol or xylenols. Fifty grams of the cresol are weighed into a small conical flask and mixed with 125 g. of sulphuric acid of sp. gr. 1.84. The temperature of the mixture rises spontaneously to between 60° and 70°, and further warming is unnecessary. After standing for one to two hours, the sulphonic acid is nitrated in a tubulated retort of 1 litre capacity, placed in a sand-bath; the neck of the retort is connected to a wash-bottle, and this, in turn, to a good draught. Four hundred c.c. of nitric acid of sp. gr. 1.38 are placed in the retort, heated to 60°, and the flame then removed. A cylindrical dropping-funnel without a neck is fixed in the tubulure of the retort by a rubber stopper, and the small conical flask in which the sulphonation was effected is placed upside-

<sup>1</sup> *Z. angew. Chem.*, 1901, 14, 157.

down over the funnel in such a way that the contents are only delivered slowly and are similarly emptied from below. The sulphonic acid is allowed to gradually drop into the hot nitric acid during a period of one and a half to two hours; it is thus completely nitrated and oxidised; the oxidation is accompanied by a violent development of heat and evolution of nitrous fumes. About twenty minutes after the conclusion of the reaction, the contents of the retort are poured into a dish containing 200 c.c. of water, and the retort rinsed out with a further 200 c.c. After standing overnight, the crystalline mass is crushed in the dish, filtered on a hardened filter on the pump, washed with a further 200 c.c. of water, and weighed. When treated in this manner 50 g. of pure *m*-cresol yield 87.8 g. of trinitro-*m*-cresol, being 175.6 per cent., whereas by Raschig's method only 174.0 per cent. is obtained on the weight of the original cresol.

H. Ditz<sup>1</sup> has described a method, based on the volumetric bromine determination of Ditz and Cedivoda,<sup>2</sup> but it is only available in the complete absence of phenol and xyenols. Ditz recommends the addition of a definite amount of *m*-cresol when using either of the above methods for cresols containing more than 10 per cent. of phenol, so as to reduce the amount of the latter below this proportion.

It is necessary occasionally to determine all three isomers in a commercial cresol. In this case Raschig<sup>3</sup> separates the *o*-cresol completely by repeated fractional distillation, and obtains a distillate containing roughly 60 per cent. of *m*-cresol and 40 per cent. of *p*-cresol, in which the *m*-compound is determined by Raschig's method.

Pure *o*-cresol, obtained from coal tar cresol by fractional distillation, is now a commercial product, and amongst other uses finds employment for the preparation of "sulphide" dyestuffs. It is tested for purity by means of its melting and boiling points.

#### (d) Carbolic Acid Preparations.

Under this heading are comprised carbolic acid and cresylic acid of various qualities, solutions of carbolic acid, of cresols, or of tar oils in soap or in other aqueous solvents (Creolin, Lysol, Sapocarbol, etc.), and disinfecting powders. Each of these classes of substances requires special analytical treatment, and very many methods have been proposed for their examination, of which the following are the most reliable. In the case of disinfectant preparations and antiseptics, usually a knowledge of the amount of total phenols present will suffice. As, however, the antiseptic power of the cresols and xyenols is considerably greater than that of phenol, it may be necessary in certain cases to obtain

<sup>1</sup> *Z. angew. Chem.*, 1900, 13, 1050.

<sup>2</sup> *Ibid.*, 1899, 12, 873, 897.

<sup>3</sup> *Ibid.*, 1900, 13, 759.



information as to the composition of the phenols present. The methods described above may then be used.

**Crude Carbolic Acid.**—The commercial qualities of crude carbolic and cresylic acids are known as 15 to 20 per cent., 25 to 30 per cent., 50 to 60 per cent., and 90 to 100 per cent. carbolic acid. The first is a distillate of coal tar, the last, usually a residue from the distillation of crude phenol, containing cresols and higher homologues, whilst the intermediate qualities are mixtures of the other two. Sometimes the 90 to 100 per cent. quality consists of crude carbolic acid from light tar oils, and contains both phenol and its higher homologues; this point is settled by the boiling point and by the amount of water present.

Both the works and the trade usually employ the following method for determining the percentage of phenols:—Ten volumes of the crude carbolic acid are shaken for a considerable time with ninety volumes of sodium hydroxide solution of sp. gr. 1.079, and after settling completely the remaining volume of oil is calculated as non-phenols. The sodium phenate solution is separated from the oil, acidified with hydrochloric acid, the phenol salted out with common salt, and the volume of crude, moist phenol read off. The volumes of phenol and non-phenols thus found should together be approximately equal to the original volume of the sample. The method is open to objections, as the solution of sodium phenate is capable of dissolving considerable quantities of tar hydrocarbons and bases, the former being thus reckoned as phenols, whilst the latter, which remain in solution on acidification, are not included in the non-phenols or in the phenols. The result would be more exact if before acidifying the sodium phenate solution the bases were distilled off in a current of steam, collected, and added to the non-phenols. The increase in volume of the separated phenol due to dissolved water about compensates for the amount of phenol remaining dissolved in the hydrochloric acid. A similar method is used by G. Schacherl.<sup>1</sup>

**Solutions containing Soap and Phenol, or Cresol.**—These comprise sapocarbol, lysol, creolin, carbolic soap, and similar preparations. They cannot be examined by the methods given above, as the fatty acids interfere, and must, therefore, be systematically separated into hydrocarbons, phenols, and fatty acids if a full analysis be required.

The methods of Allen,<sup>2</sup> T. Weyl,<sup>3</sup> Bodländer,<sup>4</sup> Otto and Beckurts,<sup>5</sup> Pfrenger,<sup>6</sup> Helbing and Passmore,<sup>7</sup> Engler and Dieckhoff,<sup>8</sup> W. Reuss,<sup>9</sup> H. Fresenius and Makin,<sup>10</sup> and Spateholz,<sup>11</sup> need not be described here,

<sup>1</sup> *Chem. Zeit. Rep.*, 1892, 16, 365; *Z. anal. Chem.*, 1901, 40, 615.

<sup>2</sup> *The Analyst*, 1886, 11, 103.

<sup>7</sup> *J. Soc. Chem. Ind.*, 1892, 11, 848.

<sup>3</sup> *Ber.*, 1889, 22, 138.

<sup>8</sup> *Arch. Pharm.*, 1892, 230, 589.

<sup>4</sup> *Reichs-Med.-Anzeiger*, 1888, Nos. 10 and 11.

<sup>9</sup> *Pharm. Zeit.*, 1894, 39, 525.

<sup>5</sup> *Pharm. Zentralb.*, 1889, p. 227.

<sup>10</sup> *Z. anal. Chem.*, 1896, 35, 325.

<sup>6</sup> *Arch. Pharm.*, 1890, 228, 701.

<sup>11</sup> *Ibid.*, 1898, 32, 58.

as Ditz and Clauser<sup>1</sup> have shown that they do not give reliable results. The errors in these methods are partly inherent and partly due to technical difficulties in carrying them out.

Ditz and Clauser analyse lysol by the following method, which is applicable also to all mixtures of phenols with fatty acids and their salts (soaps). Five grams of lysol are dissolved in 100 c.c. of lukewarm water, and 20 to 30 c.c. of 10 per cent. sodium hydroxide solution added, so that the phenols are completely converted into their alkali salts. The hydrocarbons are then extracted by shaking out two to three times with ether, which is afterwards freed from traces of dissolved phenates by shaking with dilute sodium hydroxide solution; this dilute alkali is added to the main alkaline solution. The ethereal extracts are dried with anhydrous potassium carbonate, which is afterwards washed with a little dry ether, carefully evaporated, and the residue dried over strong sulphuric acid until the weight is constant. The alkaline solution containing the phenols, etc., is freed from ether by warming on the water-bath, and neutralised with hydrochloric acid. The point of neutrality is easily recognised by the first signs of turbidity. The solution is then cooled, and treated with an excess of barium chloride and with titrated barium hydroxide solution, about equivalent in quantity to the cresol which is present. The barium oleate must be precipitated in the cold, as it otherwise separates in an unsatisfactory condition. After stirring for a short time, the liquid is filtered as rapidly as possible, in order to avoid decomposition of the cresolate and the production of turbidity in the filtrate by the carbon dioxide in the air. The precipitated barium oleate is first washed with water containing a little barium hydroxide and finally with hot, distilled water. It is then rinsed into the beaker in which the precipitation was effected, decomposed with hydrochloric acid, filtered through the same filter as before, and the fatty acid examined and estimated by any of the ordinary methods. The cresols, freed from fatty acids, are now present in the filtrate, and can be determined gravimetrically by acidifying and extracting with ether. It is more accurate to dilute the acidified filtrate to a definite volume and to determine the contained cresols by Koppeschaar's method (p. 823); several estimations should be made and the mean value taken. In this way the mean bromine value of the total phenols is obtained. As the relative proportion of the various phenols of which the mixture consists is unknown, a supplementary determination is made of the bromine-absorbing power of a weighed quantity of the mixed phenols. For this purpose a convenient quantity of the acidified filtrate is shaken out with ether, the solvent evaporated, and after drying at 100° to 110°, the residue weighed and titrated with bromine by Koppeschaar's method. Any loss of the

<sup>1</sup> *Chem. Zeit.*, 1898, 22, 732.

phenols during their isolation for this purpose is obviously of no consequence, since their relative proportion will not be affected. The percentage of phenols is then given by the formula:—

$$\frac{100 \times a \times d}{b \times c}.$$

Where  $a$  is the weight of bromine equal to the total phenols,  $d$  the weight of the phenols from the ethereal extract,  $b$  the weight of bromine absorbed by the same, and  $c$  the weight of lysol used for the analysis.

For the purposes of this determination, Koppeschaar's method must be modified by dissolving nine parts of the bromide-bromate mixture in 1000 instead of 100 parts of water; moreover, after liberating the bromine with sulphuric acid, the liquid must be allowed to stand for half an hour so that the reaction may be quite complete; also, on titrating back with thiosulphate solution, the liquid should again be allowed to stand for a quarter of an hour after decolorisation, so that the blue colour, which usually reappears, may be completely removed by further addition of thiosulphate.

M. Dayk<sup>1</sup> has proposed the following simple method for the estimation of soap in tar emulsions. A suitable quantity of the sample (about 20 g.) is placed in a beaker and treated with a known volume of warm water, and a solution of cane sugar added until a clear syrup results. The whole is warmed on the water-bath until the liquid separates into two layers, then transferred to a separating funnel whilst still warm, and the lower, aqueous solution run into a concentrated brine solution. Any soap present separates out completely and is filtered off, washed with brine solution, allowed to dry, and purified by crystallisation from alcohol.

Methods of analysis have also been described by Thresh,<sup>2</sup> O. Schmatolla,<sup>3</sup> and E. Borral.<sup>4</sup>

**Disinfecting Powders.**—These usually consist of mixtures of various inorganic materials with varying quantities of cresol, crude carbolic acid, or tar oils. Slaked lime, powdered gypsum, or levigated chalk are the ordinary mineral constituents. Less common preparations are prepared by using as carriers certain anhydrous compounds such as boric anhydride, aluminium oxide, magnesium oxide, or dehydrated salts, such as calcined borax, alum, or salts of pyro- and meta-phosphoric acids. These salts form solid addition compounds with phenols, in which the latter take the place of water of crystallisation. Other preparations are made by impregnating porous materials such as cardboard, gypsum plates, or porous earthenware with carbolic acid.

<sup>1</sup> *Corps Gras. Ind.*, 1908, No. 10.

<sup>2</sup> *Chem. and Drug.*, 1901, 59, 1123.

<sup>3</sup> *Chem. Zeit.*, 1903, 27, 634.

<sup>4</sup> *J. Pharm. Chim.*, 1903, 17, [3], 98.

The active constituents of the above-mentioned and other similar preparations, which consist of phenols and tar oils, are separated by distillation in a current of steam or by extraction with ether, after first acidifying, should basic constituents be present. They are then further examined by any of the methods described above. W. Staveley<sup>1</sup> has criticised a number of proposals in this connection, including those of R. Williams<sup>2</sup> and of Muter and de Koningh.<sup>3</sup>

E. Swoboda<sup>4</sup> uses the following method, which gives sufficiently accurate results:—Twenty grams of the sample are shaken up in a litre flask with 50 c.c. of 20 per cent. potassium hydroxide solution, the mixture allowed to stand for fifteen minutes, the contents made up to 1 litre and well mixed. After standing for some time the liquid becomes clear and the non-phenols rise to the surface. Fifty c.c. of the clear liquid are drawn off, of which the first 25 c.c. are used for a determination of the phenols by Koppeschaar's method. The percentage of active phenols in the 20 g. of the sample originally taken is found by multiplying the amount of bromine absorbed by the 25 c.c. of solution by 39.16.

### Qualitative Tests for Phenol.

The most reliable qualitative test for phenol is Landolt's well-known reaction with bromine water, which gives a white precipitate of tribromophenol.<sup>5</sup> With 1 part in 44,000 an immediate and very distinct turbidity is obtained, whilst with 1 part in 60,000 it is distinct after twenty-four hours' standing. Other phenols also give precipitates of bromophenols when treated with bromine water, but they can be distinguished from phenol itself by the different melting point of the product. Tribromophenol melts at 94° and crystallises from dilute alcohol in long, hair-fine needles. Thymol yields a turbidity immediately at a dilution of 1 in 60,000, and is thus even more sensitive to this test than phenol. Aniline and similar bases are also precipitated by bromine water, but can easily be distinguished from phenol by filtering and washing the precipitate, and warming it gently in a test tube with water and a little sodium amalgam. If the liquid is then poured into a small dish and acidified with sulphuric acid the characteristic smell of phenol becomes apparent if this was originally present.

Liebermann's reaction is also reliable.<sup>6</sup> The phenol, which has been liquefied with a trace of water, is treated with concentrated sulphuric acid containing 6 per cent. of sodium or potassium nitrite, when a brown coloration is obtained which changes to green and

<sup>1</sup> *Chem. Zeit.*, 1889, 13, 1126.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1888, 7, 826.

<sup>3</sup> *Analyst*, 1887, 12, 191.

<sup>4</sup> *Chem. Zeit.*, 1891, 15, 59.

<sup>5</sup> *Ber.*, 1871, 4, 770.

<sup>6</sup> *Ibid.*, 1874, 7, 247.

blue successively, owing to the formation of Liebermann's phenol-dyestuffs.

A very delicate test for phenol is that obtained with Millon's reagent, the limit of sensitiveness being 1 in 200,000. This reagent consists of mercurous nitrate solution containing a little nitrous acid, and was first recommended as a test for phenol by Plugge.<sup>1</sup> W. Vaubel<sup>2</sup> studied the reaction in detail, and came to the following conclusions in regard to its application:—The reagent as prepared by dissolving one part of mercury in one part of cold, fuming nitric acid or one part of nitric acid of sp. gr. 1.4, warming towards the end of the reaction, and diluting with two parts of distilled water, contains a little nitrous acid but mainly mercurous nitrate and nitric oxide, of which, perhaps, a little is converted into nitrogen dioxide by the oxygen of the air. These gases are absolutely essential for the reaction, and much warming must, therefore, be avoided during the preparation of the reagent, as they are easily driven off by heat.

Di-*o*- and di-*m*-substituted phenols do not yield the reaction; among the naphthols,  $\beta$ -naphthol alone gives a similar product,  $\alpha$ -naphthol and derivatives giving nitroso-compounds.

Almén<sup>3</sup> adds five to ten drops of Millon's reagent to 20 c.c. of the solution to be tested, boils, and removes the yellowish red turbidity of basic salts, which is usually formed, by careful addition of nitric acid. The red coloration thus produced becomes still more intense after a short time. Unfortunately the same reaction is given by salicylic acid.

In order to detect phenol in presence of salicylic acid, ammonia and sodium hypochlorite are added to the liquid. In this way 1 part of phenol in 50,000 can be detected by the blue coloration, which, however, at this dilution requires twenty-four hours' standing for its appearance.

According to J. M. Wilkie,<sup>4</sup> much the most sensitive test for phenol (also given by salicylic acid) is the formation of the very voluminous tri-iodophenol. This is carried out by adding to the solution decinormal iodine and sodium carbonate and, after five minutes, acidifying, when the tri-iodophenol is precipitated. Less than one part of phenol per million can be thus detected, whilst four parts per million gives an immediate indication.

Carletti<sup>5</sup> states that small quantities of phenol in salicylic acid or of phenates in salts of this acid may be identified by stirring together 0.25 g. with 5 c.c. of distilled water in a test tube, adding two drops of a 2 per cent. alcoholic furfural solution, and then pouring 2 or 3 c.c. of concentrated sulphuric acid down the side of the tube so that it

<sup>1</sup> *Z. anal. Chem.*, 1872, II, 173.

<sup>3</sup> *Pharm. J.*, 1887, 7, 812.

<sup>2</sup> *Z. angew. Chem.*, 1900, 13, 1125.

<sup>4</sup> *J. Soc. Chem. Ind.*, 1911, 30, 402.

<sup>5</sup> *Chem. Centr.*, 1907, II., 427.

forms a layer on the bottom. A yellow ring forms at the contact zone, above which, according to the quantity of phenol present, a deep blue ring appears, even if the contained phenol only amounts to 0.00005 g.

Endemann<sup>1</sup> evaporates a solution of formaldehyde (formalin) with phenol almost to dryness, and adds a dehydrating agent such as concentrated sulphuric acid; coloured products are obtained, probably of the triphenylmethane series, which vary in colour with the particular phenol present.

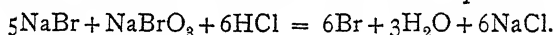
J. Herzog<sup>2</sup> recommends diphenylcarbamic chloride  $(C_6H_5)_2N.COCl$  in pyridine solution as a reagent for phenols; it produces the corresponding phenolic diphenylcarbamate.

Runge's well-known ferric chloride reaction is given by many other substances besides phenol.<sup>3</sup>

### Quantitative Estimation of Phenol.

Phenol is quantitatively determined either by the method of Koppeschaar,<sup>4</sup> which depends on Landolt's tribromophenol reaction, or by Messinger and Vortmann's method.<sup>5</sup> Both methods yield equally accurate results.

(a) **Koppeschaar's Method.**—Instead of bromine water, Koppeschaar uses a solution of sodium bromide and bromate, which evolves bromine with hydrochloric acid in accordance with the equation:—



The following stock solutions are required:—

(a) A solution of sodium thiosulphate equivalent to an iodine solution containing 5 g. of iodine per litre.

(b) A solution containing 125 g. of potassium iodide per litre.

(c) A solution of  $5NaBr + NaBrO_3$ , of such strength that 50 c.c., when mixed with 10 c.c. of the potassium iodide solution, 5 c.c. of strong hydrochloric acid, and 100 c.c. of water, will require for decolorisation 86 to 95 c.c. of the sodium thiosulphate solution. This solution is prepared by treating fairly pure sodium hydroxide solution with excess of bromine, evaporating to dryness, and powdering the residue; 9 g. of this residue are dissolved in 100 c.c. of water and diluted to the correct strength, after titration.

To carry out the estimation, 4 g. of the sample, or more in the case of preparations containing comparatively little phenol, are dissolved in a litre of water. Twenty-five c.c. of this solution are placed in a stoppered flask of about 250 c.c. capacity, 100 c.c. of the bromide-bromate solution added, followed by 5 c.c. of concentrated hydrochloric acid, the flask closed, the contents well shaken, and allowed to stand

<sup>1</sup> *Z. anal. Chem.*, 1901, 40, 667.

<sup>2</sup> *Ber.*, 1907, 40, 1831.

<sup>3</sup> Cf. Hess, *Annalen*, 1876, 182, 161; also Raschig, *Z. angew. Chem.*, 1907, 20, 2065.

<sup>4</sup> *Z. anal. Chem.*, 1876, 15, 233.

<sup>5</sup> *Ber.*, 1890, 23, 2753.

for fifteen minutes. Ten c.c. of the potassium iodide solution are then added, and the whole again shaken. The liberated iodine is then titrated with the sodium thiosulphate solution, adding starch towards the end of the operation.

If the solutions are of exactly standard strength and the operations are carried out precisely as prescribed, the percentage of phenol in the sample is given by the formula :—

$$(2a - b) \times 0.61753,$$

where  $a$  is the number of c.c. of sodium thiosulphate solution required by the bromide-bromate mixture used, and  $b$  the number of c.c. required by the final excess of bromine.

In the case of preparations containing little phenol, a multiple of 4 g. of the sample may be taken for the estimation, but in no case should 25 c.c. of the filtered liquid used for the titration contain more than 0.1 g. of pure phenol.

Beckurts<sup>1</sup> recommends the following modification of Koppeschaar's method, using the standard solutions proposed by K. Seubert.<sup>2</sup> These consist of a  $N/20$  potassium bromide solution (containing 5.939 g. KBr per litre), a  $N/100$  potassium bromate solution (containing 1.666 g. per litre), a  $N/10$  sodium thiosulphate solution, and a potassium iodide solution containing 125 g. per litre. For the estimation, 25 to 30 c.c. of the phenol solution of 0.1 per cent. strength are shaken in a stoppered flask with 50 c.c. of each of the standard bromide and bromate solutions together with 5 c.c. of strong sulphuric acid. After ten to fifteen minutes 10 c.c. of the potassium iodide solution are added, and the liberated iodine titrated with  $N/10$  thiosulphate solution, each cubic centimetre of which is equal to 0.008 g. Br or 0.00156 g. of phenol.

Koppeschaar's method cannot be used for cresols, as they absorb less bromine than phenol. Tóth<sup>3</sup> has, however, described a modification, which has been improved by Thurnauer and Stockmeier,<sup>4</sup> which allows of determinations of the phenol, cresols, etc., being carried out in about half an hour. From 1.5 to 2 g. of "Crude 60 per cent. Carbohc acid," or 1 g. of "Crude 100 per cent. Carbohc acid," are mixed in a small flask with three times its volume of 30 per cent. potassium hydroxide solution, and shaken for ten minutes. The liquid is then diluted to 1 litre, when the hydrocarbons separate readily, either on the bottom of the flask or on the surface of the liquid, partly in the solid state and partly in drops. One hundred c.c. of the aqueous liquid are drawn off and filtered, and 50 c.c. of the perfectly clear filtrate are treated in a stoppered vessel with 100 c.c. of bromate solution (containing 2.517 g. sodium bromate and 9 to 10 g. sodium

<sup>1</sup> *Arch. Pharm.*, 24, p. 561.

<sup>2</sup> *Ibid.*, 18, p. 321.

<sup>3</sup> *Z. Öst. Apoth.-Ver.*, 1884, 23, 1.

<sup>4</sup> *Chem. Zeit.*, 1893, 17, 119, 131.

bromide per litre), and 5 c.c. of fuming hydrochloric acid. After standing ten minutes, the solution is mixed with 15 c.c. of 12.5 per cent. potassium iodide solution, and the separated iodine is then titrated with standard sodium thiosulphate solution (12 to 13 g. per litre). It is advisable to add a few drops of chloroform together with the starch towards the end of the titration, as otherwise the tribromophenols tend to coagulate and enclose a little iodine. The results obtained by this modification agree well with those obtained by Tóth's original method:—

100 g. Phenol	require	510.6 g. bromine.
100 g. Cresol	„	444.4 g. „
100 g. Xylenol	„	393.4 g. „

Thus, the larger the amount of homologues of phenol, the more unfavourable will be the result of the analysis expressed in terms of phenol. This is all the more unsatisfactory, since the higher homologues, especially the cresols, have a greater antiseptic power than phenol itself.

The proportions in which the individual constituents of crude carbolic acid are present may also be determined by this method, if the alkaline phenol solution, freed from hydrocarbons by shaking out with ether before acidifying, is decomposed with acid, and the liberated phenols fractionated by distillation, and further examined as already described.

C. E. Smith<sup>1</sup> prepares mixtures of phenol with cresol and indifferent hydrocarbons for comparison, in order to be able to approximately determine the relative proportions in the crude carbolic acid under investigation. Tribromophenol separates as a very bulky, flocculent precipitate, which leaves the liquid quite clear, whilst the tribromocresols remain partly in suspension, and thus impart a milky appearance to the liquid, and partly separate in the form of small brownish spheres, which occupy comparatively little space. Thus the appearance of the precipitate shows whether the sample consists mainly of phenol or of cresols. For the actual determination, 1 g. of the sample is added to water in a 100 c.c. flask which is almost full, the whole then thoroughly shaken and filled up to the mark. The solution is filtered if necessary, and 2 c.c. mixed in a 100 c.c. cylinder with 10 c.c. of water, 12 c.c. of *N*/10 bromine solution, and 2 c.c. of concentrated hydrochloric acid. The cylinder is at once closed and the contents occasionally shaken during half an hour. Two c.c. of potassium iodide solution are then added, the whole well shaken, and finally titrated with *N*/10 sodium thiosulphate solution till colourless. If much cresol is present the liquid again becomes yellow after a short time. Thiosulphate must then be added until the liquid remains colourless after shaking and allowing to stand for some time. By subtracting the number of cubic centimetres used from 12, the number of cubic centi-

<sup>1</sup> *Amer. J. Pharm.*, 1898, 70, 369.



metres of  $N/10$  bromine solution absorbed by 0.02 g. of the sample is found. In calculating the results the following table may be used, which gives the volume of  $N/10$  bromine solution required by 0.02 g. of a mixture of 85 per cent. of mixed phenol and cresols in various proportions with 15 per cent. of tar oil:—

Mainly Phenol	.	.	.	.	.	11.00 c.c.
75 per cent. Phenol and 25 per cent. Cresol	.	.	.	.	.	10.65 "
50 " " 50 " "	.	.	.	.	.	10.30 "
25 " " 75 " "	.	.	.	.	.	9.95 "
Mainly Cresol	.	.	.	.	.	9.60 "

If, for instance, the brominated precipitate shows that phenol and cresol are present in approximately equal proportions, and 10.7 c.c. of bromine solution are used, the sample contains  $\frac{10.7 \times 85}{10.3} = 88$  per cent. of phenol and cresols. An alternative method has been described by Michonneau.<sup>1</sup>

F. Telle<sup>2</sup> uses a standardised sodium hypochlorite solution, made by diluting 35 c.c. of the solution, as ordinarily sold, to 1 litre. This is added to an acid solution of potassium bromide, and this solution used instead of the Koppeschaar or Seubert reagents.

(b) **Messinger and Vortmann's Method.**—In this method use is made of the fact that, when iodine acts on an alkaline phenol solution, six atoms of iodine are used up by each molecule of phenol. The excess of iodine is then titrated back after acidifying with dilute sulphuric acid. For the determination, from 2 to 3 g. of the phenol are dissolved in sodium hydroxide free from nitrite, at least 3 mols. of sodium hydroxide being used for each molecule of phenol. The solution is diluted to 250 or 500 c.c., and 5 or 10 c.c. of this liquid is warmed in a small flask to 60°. Standard iodine solution is then added, with shaking, until the liquid is of a deep yellow colour, and a red precipitate is formed. The mixture is cooled, acidified with dilute sulphuric acid, diluted to 250 or 500 c.c., filtered, and 100 c.c. of the filtrate titrated with  $N/10$  sodium thiosulphate solution. The amount of iodine used up, multiplied by 0.12356, gives the amount of phenol. This method is accurate, but like Koppeschaar's method, can only be employed for solutions of pure phenol, and not in the presence of homologues or of hydroxy-acids.

This method has been subjected to a careful study by J. M. Wilkie,<sup>3</sup> who has worked out the following improved procedure:—To the dilute phenol solution is added equal volumes of decinormal iodine and sodium carbonate. After five minutes, excess of sulphuric acid is added, and

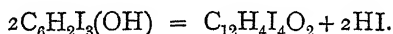
<sup>1</sup> *J. Pharm. Chim.*, 1903, 17, 161.

<sup>2</sup> *Ibid.*, 1901, 14 (7), 289.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1911, 30, 398.

the residual iodine titrated with decinormal sodium thiosulphate and starch. Should too little iodine have been added, this is indicated by pronounced fading of the brown colour due to the iodine, and in extreme cases by precipitation of tri-iodophenol; in such circumstances more iodine and sodium carbonate is to be added, and the determination completed in the usual manner, after five minutes standing. Generally not more than half the added iodine should enter into reaction. The determination is most conveniently carried out in stoppered bottles.

The whole operation is performed in the cold. The primary product of the reaction is the tri-iodophenol, but if the reaction mixture is allowed to proceed for twenty minutes before acidification, a secondary reaction takes place with production of the red coloured tetra-iodoquinone:—



R. Bader<sup>1</sup> has proposed an alkalimetric method for the estimation of phenol, and J. F. Toche<sup>2</sup> a volumetric permanganate method.

## V.—PYRIDINE BASES

The bases in coal tar belong mainly to the pyridine and quinoline series; small quantities of pyrrol and of aromatic bases, such as aniline, are also present. As this basic mixture is never worked up, being chiefly used for denaturing spirit, it is not necessary to determine the individual constituents.

In Germany<sup>3</sup> it has been decided that the mixture of bases used for denaturing alcohol should conform to the following specification:—

**Colour.**—The colour shall not be darker than that of 2 c.c. of *N*/10 iodine solution in 1 litre of distilled water.

**Reaction with Cadmium Chloride.**—One c.c. of the bases is dissolved in 100 c.c. of water, and 10 c.c. of this solution shaken vigorously with 5 c.c. of a 5 per cent. solution of anhydrous cadmium chloride. A distinct crystalline precipitate should be formed within ten minutes. Ten c.c. of the same solution of the pyridine bases should also yield a white precipitate with 5 c.c. of Nessler solution.

**Boiling Point.**—On distilling 100 volumes of the mixture at the normal atmospheric pressure of 760 mm., at least fifty volumes should distil over up to a temperature of 140° and ninety volumes up to 160°.

**Miscibility with Water.**—Twenty c.c. of the bases must not form oily drops when mixed with 40 c.c. of water.

**Content of Water.**—When 20 c.c. of the bases are shaken up with

<sup>1</sup> *Z. anal. Chem.*, 1892, 31, 58.

<sup>2</sup> *Pharm. J.*, 1901, 66, 360.

<sup>3</sup> German Confederation of 9th March 1905.

20 c.c. of sodium hydroxide solution of sp. gr. 1.4, and allowed to stand for a short time, at least 18.5 c.c. of the bases should separate.

**Titration of the Bases.**—One c.c. of the bases is dissolved in 10 c.c. of water, and normal sulphuric acid added until a drop of the mixture, when placed on Congo paper, shows a blue edge which at once disappears again. This reaction should not appear with less than 10 c.c. of normal sulphuric acid. The Congo paper is prepared by impregnating filter paper with a solution containing 1 g. of Congo red in 1 litre of water, and drying.

Pyridine bases can readily be detected in denaturated alcohol by adding a solution of mercuric potassium iodide,<sup>1</sup> which produces a yellow crystalline precipitate even in dilute solutions. The sample of alcohol is evaporated to dryness with a little sulphuric acid, the residue distilled with aqueous sodium hydroxide, and the distillate treated with the reagent. To confirm the presence of pyridine, the precipitate should be filtered off, washed, and heated with potassium hydroxide solution, when the characteristic smell of pyridine should be observed. K. E. Schulze<sup>2</sup> recommends ferric chloride as an indicator when titrating pyridine bases volumetrically, and states that all other indicators are inapplicable. He dissolves 5 c.c. of the basic mixture in 100 c.c. of water, and adds to the solution 1 c.c. of 5 per cent. ferric chloride solution, which causes the precipitation of flocculent ferric hydroxide. Normal sulphuric acid is then added until the precipitate just disappears and the liquid becomes perfectly clear; commercial samples require about 12 to 13 c.c. of the acid. The acid should be added, drop by drop, towards the end of the titration at intervals of from one-half to one minute.

The following gravimetric method of estimating pyridine in aqueous solution has been proposed by M. Francois,<sup>3</sup> who makes use of the insolubility of the gold chloride double salt in pure ether (free from aldehyde). To as much of the aqueous or hydrochloric acid solution as may be supposed to contain at least 0.1 g. of the bases, twenty to thirty drops of hydrochloric acid, and an excess of gold chloride solution are added in a small beaker. A precipitate is formed and the liquid assumes a deep yellow colour. It is evaporated to dryness on the water-bath, and after all hydrochloric acid has been driven off, is placed in a desiccator. The dry residue is then digested with pure ether, rinsed on to a filter, and washed with ether until the washings are colourless. The filter and contents are then ignited in a crucible, and the quantity of pyridine calculated from the weight of metallic gold obtained; the double salt has the composition,  $C_5H_5N.HCl.AuCl_3$ .

<sup>1</sup> *Chem. Ind.*, 1900, 23, 25.

<sup>2</sup> *Ber.*, 1887, 20, 3391.

<sup>3</sup> *Comptes rend.*, 1903, 137, 324.

## VI.—HEAVY OILS

The Heavy Oils from coal tar—*i.e.*, Heavy Oil proper, freed from other marketable products, as well as filtered anthracene oil, are employed for a variety of purposes. They occur in varying qualities and come on the market under special names, such as Creosote Oil, Oil for Fuel, Absorption Oils, Carbolineum, etc.

## (a) Creosote Oil.

Creosote oil is frequently used as a disinfectant, and is then examined by one of the methods described above, but its main use is for impregnating various kinds of wood, which have to stand exposure in the open, especially railway sleepers, telegraph poles, and the like. In the case of sleepers and construction timbers, the oil is forced into the wood with the aid of pressure or a vacuum. The consumption of creosote oil for wood preservation has become an enormous one in recent years, more especially in America. According to Church, 56 million gallons were employed in the United States for this purpose during 1909, a considerable part of which was imported from England. Tidy<sup>1</sup> has described a method of examining samples of creosote oil to be used for such purposes. It should, in general, conform to the following specification. The oil must be of such a character that on distillation a maximum of 3 per cent. distils up to 150°, a maximum of 10 per cent. up to 200°, and not more than 25 per cent. up to 235°. The sp. gr. at 15° must be between 1.04 and 1.10. At this temperature the oil must be perfectly clear. The amount of acid constituents—that is, constituents soluble in sodium hydroxide solution of sp. gr. 1.15 at 15° (phenolic substances)—must be at least 6 per cent. The oil should be quite transparent at 40°, and should remain clear when mixed with an equal volume of crystallisable benzene, without the separation of more than traces of undissolved substances.

The *Distillation Test* is carried out in a copper still or glass retort of about 300 c.c. capacity, the neck of which is attached to an adapter bent at an obtuse angle (Fig. 133).

The retort is heated on a wire gauze and the distillate collected in a 100 c.c. cylinder at the rate of about 120 drops per minute. The retort is charged with 100 c.c. of the oil by measuring off 102 c.c. and pouring it in through a small funnel; the 2 c.c. in excess remain on the sides of the measuring cylinder and of the funnel. The volume of distillate is read off at the specified temperatures without interrupting the distillation. When the temperature of 235° is reached, the burner is temporarily removed, the thermometer replaced by a good cork, and

<sup>1</sup> Cf. Lunge, *Coal Tar and Ammonia*, p. 552.

the distillation continued until 85 to 90 per cent. of the oil has been collected in the cylinder.

This distillate is used for the estimation of the tar acids, which is carried out as follows:—One hundred c.c. of a solution of sodium hydroxide of sp. gr. 1.15, which has been saturated with common salt

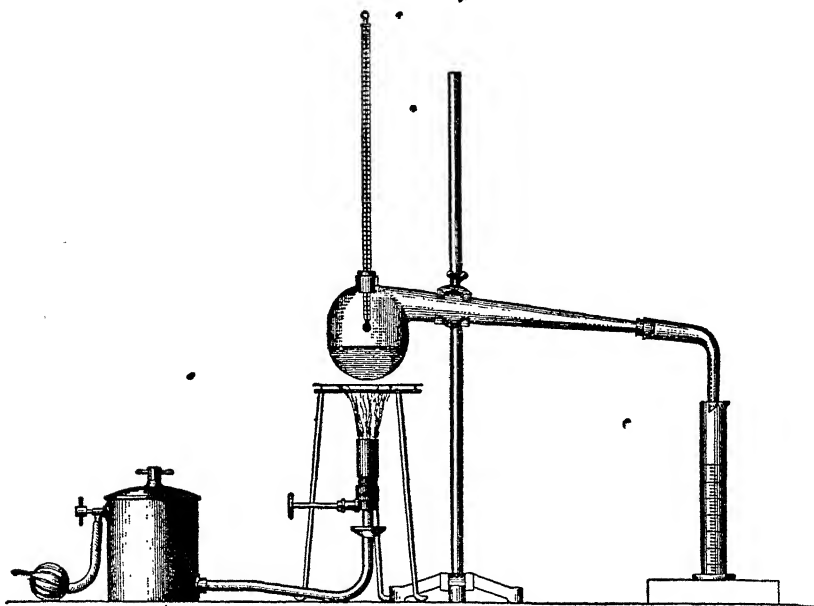


FIG. 183.

to facilitate the separation of the oil, is placed in a stoppered cylinder of 250 c.c. capacity, and the contents of the receiver added together with 25 c.c. of pure benzene used to wash out the receiver. After shaking thoroughly, the cylinder is allowed to stand for about an hour, and the increase in volume of the lower aqueous layer read off in volume percentages.

The test for solid impurities is made by first warming the oil to 45° to 50°; as soon as the temperature has fallen to 40°, 20 c.c. of the oil are removed to a test tube and shaken thoroughly with an equal volume of pure, crystallisable benzene. The solution should not be perceptibly turbid, and should not leave a distinct black spot on filter paper. The original oil should also satisfy these requirements at 40°.

In a communication to the U.S. Bureau of Forestry, T. H. Davies<sup>1</sup> prescribes the following tests as necessary for a full examination of a commercial creosote for timber preservation:—

- (1) Specific gravity at 15°-5, with a hydrometer.
- (2) Colour and

<sup>1</sup> *J. Soc. Chem. Ind.*, 1910, 29, 341.

appearance by both reflected and transmitted light. (3) Absorption spot. Six drops are allowed to fall on white blotting paper, tar, dirt, free carbon, etc., separate at the centre of the spot. (4) Tar acids, determined by shaking 25 c.c. with 50 c.c. of sodium hydroxide of sp. gr. 1.1; the increase of volume of the alkali, multiplied by 4, gives the approximate percentage of tar acids. (5) Viscosity, by noting the relative times required for 50 c.c. each of the sample and of water to run out from a pipette. (6) and (7) Loss by evaporation on exposing 10 c.c. on a 3-in. watch-glass for 24, 28, and 72 hours at the ordinary temperature, and for 4 and 6 hours at 90°. (8) Naphthalene content, by cooling to 0° the fraction distilling between 200° and 250°. (9) Flash point, by the open cup method. (10) Distillation test with 100 c.c. in a side-tube fractionating flask connected to a glass tube, 24 in. long, serving as an air condenser. The flask rests upon an asbestos board having a 2-in. hole with serrated edges, and is enclosed in an asbestos box covered at the top by an asbestos plate, having a hole for the thermometer. The oil is distilled at the rate of 2 to 3 drops per second throughout, and the thermometer is fixed so that at the commencement it just touches the surface of the oil. Fractions are collected up to 200°, 200° to 220°, 220° to 250°, 250° to 270°, and 270° to 300°. For ordinary commercial control, it would probably be sufficient to determine the specific gravity, tar acids, and naphthalene, and examine the absorption spot. Results obtained with a number of commercial samples are shown in the following table:—

No.	Sp. gr. at 15°5.	Viscosity (water=1).	Tar acids.	Distillation test.					
				Up to 200°.	200°-220°.	220°-250°.	250°-270°.	270°-300°.	Residue.
			per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
1	1.019	...	12	14	21	33	12	8	12
2	1.025	...	12	11	20	37	8	12	12
3	0.975	...	...	0	9	26	16	21	28
4	1.036	1.154	11.5	8	10	28	10	13	21
5	1.000	1.635	...	17	17	21	9	13	23
6	1.035	1.179	16	7	38	31	9	10	5
7	1.071	1.501	10	1	9	29	15	15	31
8	1.020	1.099	11	7	24	43	10	10	6
9	1.067	1.648	...	3	8	21	16	15	37
10	1.018	1.166	...	7	13	26	16	17	31
11	0.986	1.487	...	0	16	34	16	17	17
12	1.037	1.203	11	11	19	29	11	9	21
13	1.042	...	30(?)	6	8	10	8	9	59
14	0.971	...	25	0	6	35	20	20	19
15	1.033	...	20	11	41	26	8	3	11
16	0.958	1.115	6	5	15	29	13	13	25
17	0.995	1.385	18	2	7	32	17	21	21
18	1.016	1.095	0	8	9	20	17	20	26

The samples are described as follows:—No. 1. American commercial creosote distilled from a mixture of coal tar and water gas tar. No. 2. The

same (refined). No. 3. Commercial creosote with some odour of wood creosote. Nos. 4, 8, and 12. Commercial American creosote. Nos. 5 and 9. Commercial American creosote (fictitious). No. 6. Belgium creosote as imported into America. No. 7. English creosote as imported into America. Nos. 10 and 14. Commercial creosote. No. 11. Scotch creosote as imported into America. No. 15. Wood creosote. No. 15. Scotch creosote, special, imported for disinfectants. No. 16. English creosote, guaranteed pure coal tar product. No. 17. English blast furnace creosote. No. 18. "Dead oil" from water gas tar.

Creosote to be used for the manufacture of disinfectants should be free from fine carbon, tarry matter, naphthalene, and water, and should contain, at least, 10 per cent. of tar acids. For the manufacture of wood stains, it should have a specific gravity between 1.020 and 1.040, a minimum naphthalene content, and contain at least 10 per cent. of tar acids. It is not possible to draw up a general specification for creosote to be used for impregnating timber, as widely differing views are held by consumers in regard to the constituents to which the preservative action is mainly due.

Coal tar creosote has a specific gravity between 1.020 and 1.040. Blast furnace creosote is generally of low specific gravity, practically free from light oils, of low naphthalene content, and comparatively rich in tar acids. Coke oven creosote is of high specific gravity, poor in tar acids, and contains considerable quantities of naphthalene and anthracene oils. Scotch creosote is usually of low specific gravity, of very low naphthalene content, contains a fair percentage of tar acids, but also contains readily volatilised constituents and paraffin derivatives. Belgian creosote has a normal specific gravity, a rather high percentage of tar acids, and contains considerable quantities of hydrocarbons distilling below  $220^{\circ}$ ; it evaporates almost completely when exposed to the air for six hours at  $90^{\circ}$ . "Dead oil" from water gas tar closely resembles coal tar creosote, except that it is almost entirely free from tar acids.

The testing of creosote for timber preservation has also been examined by C. N. Forrest,<sup>1</sup> J. C. Mann,<sup>2</sup> S. R. Church,<sup>3</sup> and by C. E. Sage.<sup>4</sup> Mann deals particularly with the determination of naphthalene.

Dean and Bateman<sup>5</sup> have emphasised the importance of the high boiling ingredients of creosote, and have suggested a sulphonation test.

The solubility in dimethylsulphate is employed as a means of ascertaining the presence of petroleum products which are insoluble in this reagent (*cf.* p. 794).

<sup>1</sup> *J. Soc. Chem. Ind.*, 1911, 30, 193.

<sup>2</sup> *Ibid.*, 1910, 29, 732.

<sup>3</sup> *Ibid.*, 1911, 30, 191.

<sup>4</sup> *Ibid.*, 1911, 30, 588.

<sup>5</sup> *U.S. Dep. of Agriculture, Circular No. 98.*

### (b) Oil for Fuel.

This should be a heavy coal tar oil with a flash point of at least 86° (Pensky). It should not contain mechanical impurities, and no separation of solid constituents should take place at temperatures above 8°. The content of water should not exceed 0.5 per cent.

### (c) Absorption Oils.

In Bueb's process for the removal of naphthalene, the coal gas is washed with oil to prevent the blocking of gas pipes through the condensation of naphthalene vapour. The oil prepared for this purpose is made by the repeated distillation of anthracene oil, so as to remove as much as possible of the constituents boiling below 270°; it is either used alone or mixed with 4 per cent. of benzol.

The following method for the examination of these oils is adopted by Bueb:—One hundred c.c. of the sample is distilled from a boiling flask of 300 c.c. capacity provided with a two-bulb fractionating column fitted with a thermometer, and connected with a condenser having a cooling surface of 300 mm. The distillate is collected in two fractions at the rate of about one drop per second.

Absorption oils containing 4 per cent. of benzene should yield the benzene (which distils over up to 120°) as a first fraction up to 200°, together with, at most, 2 per cent. by volume of distillate, while the second fraction, boiling at 200° to 270° should amount to about 4 per cent. with a maximum of 8 per cent. The smaller the volume of distillate collected between 200° and 270° the better is the oil.

In the case of oil without the benzene admixture, the volume of the first fraction is less by 4 volumes per cent. The distillate of both kinds of oil should not deposit any naphthalene or other crystals when cooled to 0° for one hour.

Washing oil for benzol, which is used in coke oven works for the extraction of benzol from coke oven gases, is, according to Spilker, a fraction of Middle Oil. Frequently, an oil is specified of which up to 90 per cent. distils over between 200° and 300°. The distillation test is carried out in the copper still used for benzol testing (p. 784).

### (d) Carbolineum.

Carbolineum is the name given to an oil which is used for painting on wood to protect it from rotting and recently also for protecting trees. It consists of heavy coal tar oil, so-called green oil (filtered anthracene oil) to which small quantities of other wood preservatives are sometimes added, such as zinc chloride or resins (colophony). It is usually of a brown colour, but is occasionally specially coloured by the addition of



aniline dyes soluble in oil. "Carbolineum Avenarius" (trade mark) is a product manufactured by R. Avenarius<sup>1</sup> by the action of chlorine on the oil.

Carbolineum is often imitated by substituting other mineral oils, even oil tars, which do not, however, exert nearly so powerful a preservative action as anthracene oil. According to Holde,<sup>2</sup> the oils described as carbolineum for impregnating wood are, as a rule, greenish black, heavy, coal tar oils having the following properties:—

Sp. Gr.	. . . . .	1.1
Viscosity at 20°	. . . . .	8 to 14
Flash point (Pensky)	. . . . .	over 100°
Distillation begins at	. . . . .	200°
Ash, per cent.	. . . . .	0.7 to 0.08

The commercial varieties of carbolineum possess the following properties:—

	Carbolineum Avenarius.	Ordinary Commercial Carbolineum.
Sp. Gr. at 15°	1.128	1.075 to 1.130
Distillation begins at	over 200°	200° to 270°
Distillate up to 200°, vol. per cent.	0	traces
" 200° to 230°, vol. per cent.	0	4 to 5
" 230° to 270°	10	2 to 15
Residue	Oil	Oil

Filsinger<sup>3</sup> has carried out comparative investigations of the various commercial qualities.

Hondurek<sup>4</sup> specifies the following properties for carbolineum:—Specific gravity, not below 1.120; boiling point, not starting below 230°; viscosity, as high as possible; flash point, above 120°; reddish brown in colour and free from solid sediment.

## VII.—PREPARED TAR (ROOFING TAR, BLACK VARNISH, ETC.)

The following reliable method of examining prepared tars is due to Lunge; it comprises determinations of specific gravity, viscosity, and quantity of volatile matter.

**Specific Gravity.**—As described on p. 757.

**Viscosity.**—This determination is made by means of Lunge's "tar-tester," Fig. 134, which is made of thick-walled glass, weighs about 39 g., and has a scale of specific gravities from 1.050 to 1.400 on the narrow portion. The instrument is used in the same manner as an ordinary hydrometer, excepting that it is not allowed to sink into the liquid till in stable equilibrium, but only till it reaches a certain point which lies sufficiently below that corresponding to the specific gravity of the tar; for this purpose, the point 1.250 has been chosen as a

<sup>1</sup> Ger. Pat. 46021.

*Mineralöle und Fette*, 1905, p. 397.

<sup>3</sup> *Chem. Zeit.*, 1891, 15, 541.

<sup>4</sup> *Oest. Chem. Zeit.*, 1904, p. 366.

practical figure. The determinations are made at a definite temperature, usually at  $15^{\circ}$ , and the tar as measured must be brought to within at least half a degree of this temperature by a standardised thermometer. Before the actual determination, the tar must be well mixed by thoroughly stirring up with a wire stirrer. The tar-tester is most conveniently suspended above the cylinder containing the tar by means of a spring clip. The instrument is first dipped into the tar up to the mark 1.250, withdrawn, and suspended for three minutes by the clip to drain, as there is a difference of several seconds in the rate at which a clean instrument and one covered with tar sinks in the same tar. As it is necessary to take several readings, it is simpler to use an instrument which has been merely drained in this way than to clean it each time. The tester is then held so that its lower end just touches the tar and is allowed to sink by its own weight, the time taken to reach the 1.250 mark being noted by means of a watch with a seconds hand. It sinks very rapidly until the wide portion is immersed, then more slowly. If the instrument leans to one side and touches the wall of the cylinder, it may be righted by a gentle touch from the side without causing appreciable error, provided that all downward pressure is avoided. Three or four determinations should always be made, the instrument being allowed to drain for two to three minutes between each, and they should agree to within two to three minutes. By allowing the instrument to sink until it comes to rest, a determination of the specific gravity of the tar may be made at the same time, but it is not so exact as the method described.

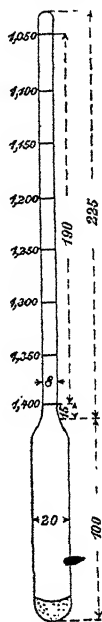


Fig. 184.

**Volatile Constituents.**—This determination is carried out by distilling 100 g. of the tar from a tubulated hard glass retort, wrapped in asbestos paper. The distillation is conducted over a naked flame, and the distillate collected in a graduated cylinder. A thermometer cannot well be used as a check on the distillation, as many of the constituents of the tar have a very high boiling point, especially if anthracene oil has been used in its preparation. It is distilled down to medium hard pitch, a point which is attained with certainty by repeating the determination two or three times with fresh quantities of tar. After cooling, the retort is broken, and the specific gravity and softening point of the pitch determined. A determination of the specific gravity of the distillate is also made. By determining the boiling point, percentages of naphthalene, phenols, etc., in the distillate, by the methods already described, it can be characterised as light oil, creosote oil, or anthracene oil (green oil).

Methods for distinguishing between prepared tar and gas tar have also been described.<sup>1</sup>

### VIII.—PITCH

Coal tar pitch is used as a binding material in the manufacture of briquettes, for asphalt manufacture, roadmaking, and other purposes. Its examination may include determinations of the specific gravity, free carbon, mineral impurities, softening and melting points, and (according to Muck) the coking-residue.

According to Spilker, a good pitch for the manufacture of briquettes should not contain more than 0.5 per cent. of ash, the softening point should not be below 60° nor above 75°, from 70 to 75 per cent. should dissolve in aniline or pyridine bases, and the coking-residue should not exceed 45 per cent.

**Specific Gravity.**—This is determined by any of the methods usual for solids. Since many samples of pitch are porous or contain air cavities (especially hard pitch), they are best examined in the form of powder. The approximate specific gravities are:—

Soft pitch . . . . .	1.250 to 1.265
Medium soft pitch . . . . .	1.275 „ 1.280
Hard pitch . . . . .	1.285 „ 1.330

**Free Carbon** is determined by extraction with aromatic hydrocarbons, as described under the examination of tar (p. 759).

**Ash** is determined in the usual manner by ignition in a porcelain crucible, finally using a muffle, as the coke is only completely burnt with some difficulty.

Muck<sup>2</sup> recommends carbonisation in a crucible, and the examination of the coke residue, as an especially useful test of the suitability of pitch for briquetting purposes. According to his view the actual quantity of coke obtained is of no consequence, but its physical condition is important; the coke may be either porous or sintered, and the behaviour of the briquette when burnt depends upon the character of the pitch from this standpoint. A briquette which crumbles in the fire, and finally bursts into fragments, owes this behaviour to the pitch which it contains becoming viscous when melted. Pitch which becomes thin on melting allows the gases and vapours which are evolved to escape quickly and easily, without disintegrating the briquette. Therefore, a pitch which forms a porous coke residue, as is the case with hard pitch containing much free carbon, and also with the soft blast furnace pitch collected from the walls of the furnace-gas mains, is not suitable for use in briquette manufacture.

<sup>1</sup> Cf. *Chem. Centr.*, 1900, ii., 595.

<sup>2</sup> *Z. Berg-, Hütten-, u. Salinenwesen im Preuss. Staat*, vol. 37.

Fuller information on this subject is given in the works of Gurlt<sup>1</sup> and of Preissig.<sup>2</sup>

**Softening and Melting Points.**—As a preliminary test, a small piece of the pitch is kneaded between the teeth when it attains the temperature of the mouth. Soft pitch is easily flattened out thus; medium hard pitch requires some pressure from the teeth, and is only worked with difficulty, whilst hard pitch grates between the teeth and falls to powder.

In the majority of cases this test is sufficient, and gives, with a little practice, fairly reliable results. Testing by means of a thermometer is, however, more reliable, and is carried out differently in different works. In English and German works flat pieces of the pitch to be tested, about 4 to 5 mm. thick and of any width, are suspended by a wire or thread in a beaker with water at the same height as the bulb of a thermometer, and carefully heated by a small flame so that the temperature of the water rises only 2° to 3° per minute. From time to time the piece tested is taken out, and tried between the fingers, and the temperatures corresponding to the following conditions noted:—

*The Softening Point*, at which the pitch can be twisted about its axis without breaking.

*More Marked Softening Point*, at which it can be moulded into any shape with very little pressure.

*Melting Point*, when it drops from the wire.

Other forms of apparatus for the determination of the softening point of pitch have been described by Lunge,<sup>3</sup> F. Muck,<sup>4</sup> E. Schenk zu Schweinsberg,<sup>5</sup> I. Klimont,<sup>6</sup> and I. Kovács.<sup>7</sup> According to P. Kraemer and C. Sarnow,<sup>8</sup> the majority of these methods of estimating the melting and softening points are unreliable, as the results depend too much upon the individuality of the experimenter, so that differences of from 5° to 10° frequently occur. The same defect arises with Engler's viscosimeter, the accuracy of which is impaired by the adhesion of the substance to the walls of the outlet. Those methods which depend upon the timing of the sinking of a heavy body into the sample, melted by the application of heat, are much better. Reliable results are obtained by the following method, which has always proved satisfactory during a long series of tests:—About 25 g. of the pitch or asphalt to be tested are put into a small tinplate vessel with a flat bottom, and melted at about 150° in an oil-bath of the form shown in Fig. 135.

<sup>1</sup> *Die Bereitung d. Steinkohlenbriketts*, Brunswick, 1880.

<sup>2</sup> *Die Presskohlen-Industrie*, Freiberg i. S., 1887.

<sup>3</sup> *Coal Tar and Ammonia*, p. 465.

<sup>4</sup> *Z. anal. Chem.*, 1890, 29, 103.

<sup>5</sup> *Z. angew. Chem.*, 1890, 3, 704.

<sup>6</sup> *Ibid.*, 1900, 13, 761.

<sup>7</sup> *J. Soc. Chem. Ind.*, 1902, 21, 1077.

<sup>8</sup> *Chem. Ind.*, 1903, 26, 55.

The depth of the molten pitch should be about 10 mm. One end of a glass tube, about 10 cm. long and 6 to 7 mm. bore, with both ends open, is dipped into the pitch, and the upper end closed with the finger upon removing it, so that the bottom end remains full of pitch; it is then allowed to cool in a horizontal position. As soon as the

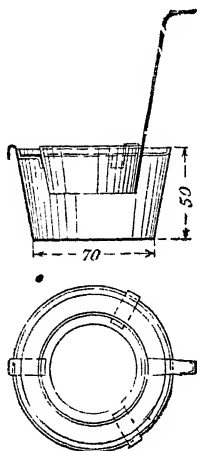


Fig. 135.

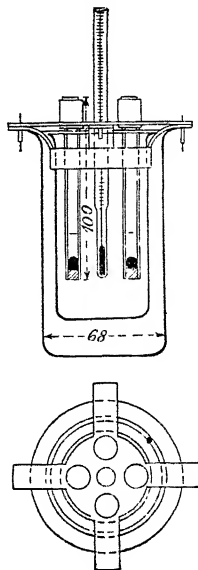


Fig. 136.

pitch ceases to run, the portion sticking to the outside of the tube is gently removed with the finger. The height of the pitch in the tube will now generally be about 5 mm. About 5 g. of mercury are then poured on to the pitch in the tube, and the tube suspended in a beaker filled with water, which is itself suspended in a second beaker filled with water, as shown in Fig. 136. A thermometer is fitted in the inner beaker so that the bulb stands at the same height as the level of the pitch in the glass tube. The whole is heated over a moderate flame, and the temperature at which the mercury breaks through the pitch is taken as the melting point of the pitch or asphalt.

By means of this apparatus several melting point determinations can be made together. In the case of asphalt of which the melting point is higher than  $90^{\circ}$ , it is advisable to fill the outer beaker with white paraffin or paraffin oil and the inner beaker with a saturated solution of common salt or magnesium chloride.

The melting points obtained by this method are several degrees lower than those found by the methods more generally used. They are to some extent influenced by the diameter of the tube, the thickness of the layer of pitch, and the depth of the column of mercury; if the

same amount of mercury be always taken, a greater diameter of the tube is compensated for by the smaller depth of mercury; the influence of the thickness of the layer of pitch is not appreciable within certain limits; for instance, thicknesses of 5, 6, and 7 mm. of the pitch gave melting points  $61^{\circ}5$ ,  $60^{\circ}5$ , and  $61^{\circ}5$ , respectively.

The following comparative determinations by different observers show that the results obtained by this method are quite reliable:—

Origin.	Soft Pitch.	Medium Pitch.	Hard Pitch.
	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$	$^{\circ}\text{C.}$
Grabow i. M. . . .	51.0	63.5	80.0
" . . . .	51.5	63.5	80.0
" . . . .	51.5	63.2	80.3
" . . . .	51.3	69.0	80.5
Niederau i. S. . . .	...	...	83.0
Passing " . . . .	...	...	84.0
" . . . .	...	...	83.5
Erkner . . . .	50.0	61.5	84.5
" . . . .	50.5	61.5	87.0
" . . . .	50.5	60.5	86.0
" . . . .	51.0	61.5	87.0

Another method, recommended by F. G. Holmes,<sup>1</sup> is to attach samples of the pitch to wires by heating the wire and inserting the end in a piece of about  $\frac{1}{2}$  in. cube. The wires are then hung by the side of a thermometer in a beaker containing 500 c.c. of water, which is heated at the rate of about  $5^{\circ}$  per minute. The melting point is the temperature at which the lump of pitch drops off the wire. The softening point, or temperature at which the lump can be twisted fairly readily, is also determined at the same time. The indications of this method are higher than those of the preceding.

O. Binder<sup>2</sup> rejects the melting point estimation as unreliable, and recommends a working test for the valuation of briquette pitch, which, he states gives very satisfactory results. His views are based on the fact that pitch, strictly speaking, possesses no definite melting point, but passes quite gradually from a brittle into a soft condition, and then into the liquid state. A small briquette press (Fig. 137), similar in construction to those used on the large scale, serves for the preparation of small test briquettes. The apparatus consists of the cylinder A, with the smoothly bored central cavity C, which is surrounded by six smaller bore-holes g, which serves as heating channels. A perforated circular pipe O, fixed under the cylinder A, is connected with the gas supply and used for heating. The cylinder A, rests on the support d, and carries centrally the block P, which exactly fits the cylinder space C. The stamp B (shown at the side in the figure) fits exactly in the

<sup>1</sup> Cf. Lunge, *Coal Tar and Ammonia*, p. 464.

<sup>2</sup> *Österr. Zeit. Berg. Hüttenwesen*, 1899, p. 279; *Chem Zeit. Rep.*, 1899, p. 194.



determining the viscosity of pitch-like substances. Their apparatus consists of a vertical shaft rotating in ball bearings, and provided at its upper end with a small wheel wound round with a cord fastened to a driving weight, which serves to produce a rotation at constant velocity. On the lower end of the shaft is a rectangular socket in which fits one of the rectangular ends of a cylindrical rod of the material to be examined, the other end being fixed in a similar but rigid socket at the foot of the apparatus. A jacket surrounds the test-piece, so that determinations may be made at various temperatures. The amount of torsion can be read off on a graduated disc fixed on the shaft.

The following formula has been deduced for the coefficient of viscosity :—

$$\mu = \frac{2 T}{\pi \cdot V \cdot R^4}$$

where T is the torsion applied, U the relative angular velocity of the cylinder per centimetre of its length, and R its radius.

The following values were obtained, with a material sold as "British Pitch" :—

Temperature.	Coefficient of Viscosity.
0°	$5.1 \times 10^{11}$
8°	$9.9 \times 10^{10}$
15°	$1.3 \times 10^{10}$

Constam and Rougeot<sup>1</sup> have given special attention to the valuation of coal tar briquettes and of briquette pitch. Their proposed method of determining the soluble constituents by extraction with carbon bisulphide is hardly practicable in works, as it requires from four to five days. Aniline and pyridine bases are much better solvents for these substances, and enable them to be completely extracted in a very short time. The same authors propose to determine the pitch contained in briquettes by extraction with carbon bisulphide; since, however, the constituents of coal tar pitch soluble in carbon bisulphide vary within wide limits (from 60 to 95 per cent.), and on the other hand finely divided coal contains up to 1 per cent. of soluble constituents, the method, even according to Constam and Rougeot's own experiments, can make no claim to accuracy, especially if the pitch content of the briquettes is considered, which as a rule varies between 5 to 8 per cent.

K. Leo<sup>2</sup> has, therefore, worked out a colorimetric method suitable for use in briquette factories, by which this important question for briquette manufacturers can be easily and quickly decided. The principle is the same as in Holde's method of testing benzine for coal tar benzol, *i.e.*, it depends upon the brown coloration of benzol

<sup>1</sup> *Glückauf*, 1906, 42, 481; *J. Soc. Chem. Ind.*, 1906, 25, 631.

<sup>2</sup> *Chem. Zeit.*, 1909, 31, 359.



in presence of pitch, which is the more intense the greater the quantity of pitch dissolved.

The analysis is carried out as follows:—If it be required to determine the average pitch contents of the briquettes manufactured during a certain period, samples are taken at intervals of the coal and ground pitch before mixing, and of the briquette charge as it leaves the stove. The separate samples are powdered and thoroughly mixed, and an average sample of from 500 g. to 1 kilo is then obtained by division. The coal and the briquette mixture are dried at 100° to determine moisture. After drying, both are reduced to the finest possible powder. To obtain a satisfactory smaller average sample of the pitch, the above sample is powdered as finely as possible, mixed, and about 50 g. weighed off. This quantity is placed in an enamelled beaker of about 250 c.c. capacity, melted in an oil-bath at 150°, thoroughly stirred with a glass rod, and allowed to solidify. When the contents of the beaker are completely solid, the oil-bath is again heated until the cake of pitch can be lifted out by a glass rod attached to it. When cold, the cake is broken up in a porcelain mortar and reduced to an evenly fine powder.

The following solutions for comparison are then made with the samples thus prepared: (i.) A standard pitch solution. To prepare this, 0.05 g. are weighed off exactly and 0.95 g. of the finely powdered coal added. This 1 g. portion containing 0.05 g. pitch, and corresponding, therefore, to a briquette sample with 5 per cent. of pitch, is introduced quantitatively into a boiling flask of 500 c.c. capacity, which must be thoroughly dry inside, and the powder evenly distributed on the bottom of the flask; 200 c.c. of colourless benzol (*e.g.*, purified 90 per cent. commercial benzol) are then added and the flask closed with a cork. (ii.) Briquette solution; 1 g. of the finely powdered briquette sample contained in a similar flask is treated in the same way as the pitch.

Both the solutions are now heated gradually to boiling under an inverted condenser. To avoid violent boiling, a second wire gauze, covered with asbestos, is placed below that supporting the flasks, so that a layer of air 1 cm. deep is between the two. After boiling for exactly half an hour, the solutions are allowed to cool, to avoid evaporation, and about 50 c.c. of each quickly filtered off into a dry flask which is immediately stoppered; to obtain a perfectly clear filtrate, a double filter is used which must fit the funnel exactly. Eggertz tubes of 20 c.c. capacity divided into  $\frac{1}{10}$ ths are employed to compare the two filtrates. Care must be taken that these tubes have the same internal diameter, and that the stoppers are well ground in. About 20 c.c. of the standard pitch solution is poured into one tube, which is then stoppered, and into the other tube exactly 10 c.c. of the briquette solution; if the latter is the darker in colour, benzol is added

until, after shaking well, it appears the same colour as the pitch solution. If, for instance, this point is reached when 4 c.c. of benzol have been added, the reading of the tube will be 14 c.c. The solution contained, therefore,  $\frac{4}{10}$ ths more pitch than the briquette solution; consequently, the percentage of pitch in the briquette sample was 7 per cent., *i.e.*, it is only necessary to divide the number of cubic centimetres by 2 to obtain the percentage. If 5 c.c. are originally used instead of 10, the number of cubic centimetres obtained gives the percentage directly.

The distinction between coal tar pitch of different origins (gas tar, coke oven tar, and blast furnace tar) is easily ascertained by determining the free carbon and the ash. Gas tar pitch (except pitch from vertical retort tar, which in this respect is similar to pitch from coke oven tar) seldom contains less than from 25 to 30 per cent. of fixed carbon; coke oven tar pitch, as a rule, from 5 to 7, rarely above 10 to 12 per cent.

Buchanan<sup>1</sup> states that the origin of a coal tar pitch can be deduced with certainty from the results of an ash determination. Blast furnace pitch contains from 6.8 to 11.1 per cent. of ash, whilst pitch from gas tar or coke oven tar scarcely ever yields more than 0.1 per cent. If a coal tar pitch yields less than 1 per cent. of ash it is almost certainly not blast furnace pitch. Blast furnace pitch is of but little value for most purposes, on account of its want of tenacity and elasticity.

Coal tar pitch can easily be distinguished from other varieties, such as pitch from lignite, wood tar pitch, or stearin pitch, by heating the sample over a naked flame. The smell so obtained is quite characteristic for each variety; that from tar pitch is reminiscent of the particular tar, and that from stearin pitch resembles that of burning fat. The behaviour with petroleum benzine may also be used; coal-tar pitch is almost insoluble, whilst pitch from lignite tar is nearly completely soluble.<sup>2</sup>

The solubilities of wood tar pitch and stearin pitch in the same solvent are given in the following table,<sup>3</sup> due to Davies:—

	In Petroleum Benzine.		Ash.	Sulphur.
	Soluble.	Insoluble.		
	Per cent.	Per cent.	Per cent.	Per cent.
Wood-tar Pitch, 1 . . .	24.44	75.56	0.20	0.69
" " 2 . . .	18.70	81.30	1.06	0.41
" " 3 . . .	15.36	84.14	0.48	0.59
Stearin Pitch . . .	71.05	28.95	5.50	0.04

<sup>1</sup> *J. Soc. Chem. Ind.*, 1894, 13, 1098.

<sup>2</sup> Scheithauer, Muspratt's *Handbuch der technischen Chemie*, 4th ed., vol. vi., p. 1982.

<sup>3</sup> *Chem. and Drug.*, 1883, 25, 504; *Cf.* also Donath and Margosches, *Chem. Ind.*, 1904, 27, 220; and Graefe, *Chem. Zeit.*, 1906, 28, 298.

The differentiation of coal tar pitch from natural asphalt and its detection in mixtures with the latter is treated of at length in H. Köhler's book, *Chemie und Technologie der natürlichen und künstlichen Asphalte*, 1904, pp. 346 *et seq.*, in which further details on the examination of coal tar pitch, with special reference to the asphalt industry, are also given.

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# ORGANIC DYES

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## I.—SYNTHETIC ORGANIC DYES

### PART I

#### RAW MATERIALS AND INTERMEDIATE PRODUCTS EMPLOYED IN THE COAL TAR INDUSTRY

##### A. RAW MATERIALS OBTAINED FROM COAL TAR

The starting-point for the manufacture of coal tar colours is the tar obtained as a by-product in the manufacture of illuminating gas and coke. This by-product is submitted in the tar distilleries to a preliminary separation into its chief constituents, which are then worked up for the manufacture of dyes, partly in the dyeworks, partly in other factories (aniline works, anthracene refineries).

##### I. Benzene, $C_6H_6$ .<sup>1</sup>

Benzene, one of the most important substances in the colour industry, is, in the pure state, a colourless liquid, boiling point  $80^{\circ}5$ , sp. gr. 0.899 at  $0^{\circ}$ , and 0.8759 at  $22^{\circ}$ .<sup>2</sup> It solidifies in the cold to a crystalline mass, melting at  $5^{\circ}4$ . Benzene and water are mutually miscible to a slight extent. A change of volume does not take place when water is mixed with a quantity of benzene sufficient to saturate it. The mixture has a sp. gr. of 0.9979 at  $22^{\circ}$ , and contains 0.082 volumes of benzene per 100 volumes of water. When, however, benzene is mixed with water, a contraction is observed, 1000 c.c. of benzene and 2.11 c.c. of water occupying 1001.35 c.c. The mixture has a sp. gr. of 0.8768 at  $22^{\circ}$ , and contains 0.211 volumes of water per 100 volumes of benzene.

The technical name "benzene" denotes products of varying quality. The pure hydrocarbon is generally termed "benzene," and the commercial products which consist of benzene and its homologues,

<sup>1</sup> Cf. this Vol., p. 779.

<sup>2</sup> W. Herz, *Ber.*, 1898, 31, 2669.

"benzols." For the purposes of the colour industry, the following are of importance:—

*Almost chemically pure Benzene* ("pure Benzene"), as employed in the preparation of resorcinol, pure nitrobenzene, etc., distils within  $0^{\circ}\cdot5$ , solidifies on cooling to a white, crystalline mass, and should not contain either carbon bisulphide or hydrocarbons which cannot be nitrated.

*Ninety per cent. Benzol and 50 per cent. Benzol* are mixtures of benzene and its homologues, their compositions being such that ninety and fifty volumes per cent. respectively distil up to  $100^{\circ}$ . On distilling the residue, the temperature should not exceed  $120^{\circ}$ .

In addition to the preceding, the terms *light* and *heavy* benzol are used. (These terms refer to the boiling point, and not to the specific gravity.)

The benzols occurring in commerce are mostly the 50 per cents. and 90 per cents. These show approximately the following behaviour on distillation:—

*Volume per cent.*

	50 per cent. Benzol.	90 per cent. Benzol.
Up to $85^{\circ}$	0	20
„ $90^{\circ}$	5	52
„ $95^{\circ}$	25	12
„ $100^{\circ}$	20	6
„ $105^{\circ}$	14	5
„ $115^{\circ}$	17	3
„ $120^{\circ}$	13	0
Total	94	98

Evidently these figures do not in any way represent the actual content of benzene. In addition to this hydrocarbon, these benzols contain toluene, the xylenes, and higher aromatic hydrocarbons. Formerly they were employed directly for the preparation of the aniline oils, "aniline for red" (*i.e.*, for the manufacture of magenta) being obtained from 50 per cent. benzol and "aniline for blue" (*i.e.*, for the manufacture of spirit and soluble blues) from 90 per cent. benzol. Now the purity of the aniline oils must satisfy more stringent demands, and the crude benzenes, therefore, are submitted to a preliminary very careful fractional distillation.

Benzene, which is to serve for the manufacture of "aniline for blue," must distil constantly within  $0^{\circ}\cdot5$ , and must not develop more than a faint coloration when shaken with concentrated sulphuric acid.

The crude mixture of benzene and toluene is rarely used for the manufacture of "aniline for red"; usually these hydrocarbons are separated from one another and converted into aniline

and toluidine, which are then mixed in the requisite proportions. For this purpose, however, the purification of the hydrocarbons need not, as a rule, be carried out very carefully. Crude benzene always contains thiophen and its homologues, which were formerly overlooked but now for the most part are removed by treatment with concentrated sulphuric acid.

The first runnings of a benzene distillation (substances boiling below  $80^{\circ}$ ) contain carbon bisulphide, acetonitrile, acetone and other ketones, and aliphatic hydrocarbons.

For the detection and estimation of carbon bisulphide in commercial benzol, see this Vol., p. 795, and of thiophene, p. 797.

#### *Detection of Aliphatic Hydrocarbons.*

The higher aliphatic hydrocarbons have nearly the same boiling points as benzene and its homologues, and occasionally occur mixed with these. They are most easily detected by the fact that they cannot be nitrated. When a crude benzol is treated with nitric and sulphuric acids, all the aromatic hydrocarbons are converted into high boiling nitro-derivatives, from which the unchanged fatty hydrocarbons are readily separated by distillation. See this Vol., p. 793, for further details of the detection of petroleum benzine in coal tar benzene.

For the fractional distillation a distilling flask is used, which is connected to a condenser or simply to a glass tube, and is fitted with a thermometer, the bulb of which is placed just below the side tube of the flask, as shown in Fig. 139. One hundred c.c. of benzol are heated slowly, the temperature at which the first drops pass over being noted, and the distillation continued at such a rate that the condensed liquid falls in single drops. The distillate is received in a 100 c.c. measuring cylinder in which readings are taken at every  $5^{\circ}$ .

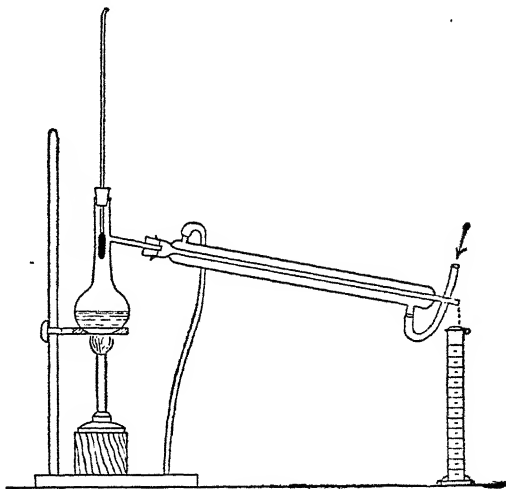


FIG. 139.

## 2. Toluene, $C_7H_8$ .

Pure toluene is a colourless liquid, boiling point  $111^{\circ}$ , sp. gr. 0.882 at  $0^{\circ}$ , and 0.872 at  $15^{\circ}$ . It solidifies at about  $-98^{\circ}$  (distinction from

benzene), and dissolves completely when shaken with concentrated sulphuric acid and warmed. In the colour industry it serves for the preparation of the nitrotoluenes, the toluidines, benzyl chloride, benzyldiene chloride, benzotrichloride, and indirectly of benzaldehyde and benzoic acid.

For its examination a determination of the boiling point and a fractional distillation (see Benzene) must be made. Pure commercial toluene must distil within  $1^{\circ}$ .

### 3. Xylene, $C_8H_{10}$ .

Three isomeric xylenes are known :

I. *o*-Xylene.—A colourless liquid, boiling point  $141^{\circ}$  to  $142^{\circ}$ , is completely oxidised by chromic acid, and is oxidised by dilute nitric acid to *o*-toluic acid, melting at  $102^{\circ}$ .

II. *m*-Xylene.—A liquid, boiling point  $139^{\circ}$ , is not attacked by dilute nitric acid, and is oxidised to *isophthalic* acid by chromic acid.

III. *p*-Xylene.—A colourless crystalline substance, melting point  $15^{\circ}$ , boiling point  $137.5$  to  $138^{\circ}$ . It is oxidised to *p*-toluic acid (melting at  $178^{\circ}$ ) by dilute nitric acid, and to *terephthalic* acid by chromic acid.

The xylene obtained from coal tar by fractional distillation is a mixture of the three isomerides. The predominating constituent, however, is always *m*-xylene, which comprises nearly 75 per cent., whilst *p*-xylene is present to the extent of some 20 per cent., and *o*-xylene at most to a few units per cent.

For the separation of the three xylenes from one another, see this Vol., p. 791.

Xylene is used for the preparation of the xylidines which are employed on the large scale. For its examination, the boiling point is determined. Commercial xylene distils within  $2^{\circ}$ .

### 4. Naphthalene, $C_{10}H_8$ .

In the pure state naphthalene forms large, colourless, crystalline leaflets with a peculiar, unpleasant odour. Its specific gravity is 1.158 at  $18^{\circ}$ , melting point  $79.2$ , boiling point  $218^{\circ}$ ; it sublimes, however, even at the ordinary temperature. It is insoluble in water, and sparingly soluble in light petroleum, but dissolves easily in benzene or hot alcohol.

Naphthalene is employed in the colour industry for the manufacture of mono- and di-nitronaphthalenes, naphthylamines, naphthols, dihydroxynaphthalenes, aminonaphthols, and phthalic acid.

It is put on the market in an almost chemically pure state. It must be quite white and must volatilise without residue, show the correct melting point, and distil almost entirely within  $1^{\circ}$ . It ought

to give only a faint coloration when shaken with concentrated sulphuric acid. For further details, see this Vol., p. 802.

### 5. Anthracene, $C_{14}H_{10}$ .

Pure anthracene forms colourless plates with a fine blue fluorescence, melting point  $216^{\circ}55$ , boiling point  $351^{\circ}$ . It is insoluble in water, and sparingly soluble in alcohol, ether, light petroleum, or cold benzene, but dissolves easily in boiling benzene and in glacial acetic acid. It forms with picric acid a compound which separates from benzene in red needles, melting at  $170^{\circ}$ . When a solution of anthracene in benzene is exposed to sunlight for a long time, it is changed into a polymeride, dianthracene, melting point  $244^{\circ}$ , which is almost insoluble in benzene. Oxidising agents convert anthracene into anthraquinone.

As the source from which synthetic alizarin is manufactured, anthracene constitutes one of the most important raw materials of the coal tar colour industry. The purity of the commercial article varies to an extraordinary extent. Its analysis is described on p. 804. The qualitative examination must include the test for carbazole, the presence of which is very detrimental in the manufacture of alizarin, and is shown by the green coloration produced when commercial anthracene is dissolved in a mixture of nitric and sulphuric acids.

### 6. Nitrobenzene, $C_6H_5NO_2$ .

The nitrobenzene employed in the coal tar colour industry now generally consists of the pure product. Formerly a distinction was drawn between light and heavy nitrobenzene (these terms refer to the boiling point and not to the specific gravity), the first name denoting almost pure nitrobenzene, the latter a mixture of this with nitrotoluene and higher homologues. Pure nitrobenzene is prepared from pure benzene, and serves for the manufacture of aniline, benzidine, metanilic acid, and nigrosine.

Pure nitrobenzene is a colourless, highly refractive liquid with an odour of oil of bitter almonds; sp. gr. 1.209 at  $15^{\circ}$ , boiling point,  $205^{\circ}$ . Friswell<sup>1</sup> gives  $D_4^{37.8}$  1.222,  $D_4^{18.7}$  1.2116,  $D_4^{28}$  1.1931, and boiling point  $209^{\circ}$  (corr.) at 760 mm. It solidifies in the cold to a crystalline mass, melting at  $3^{\circ}$ . It is practically insoluble in water, and is miscible in all proportions with alcohol, ether, or benzene. It is converted into aniline by most reducing agents such as tin and hydrochloric acid, iron, and acetic acid, etc., into azobenzene by alkali hydroxides and zinc dust, and into phenylhydroxylamine by careful reduction with zinc dust and water or by sodium amalgam.

In the examination of the commercial product, the boiling point is

<sup>1</sup> *J. Chem. Soc.*, 1897, 71, 1013.



of chief significance. During the distillation, superheating must be carefully avoided, since explosions occasionally occur.

Some samples of nitrobenzene gave the following relations between the boiling points and the specific gravities:—

Spec. Grav. at 15°.	Per cent. distilling at			Total.
	204°	206°	208°	
1·209	2	86·2	6·8	95
1·2084	12	82	8·5	97·5
1·2076	...	80	15	95

Nitrobenzene, which is used for the manufacture of aniline, must distil, however, almost completely within 1°.

### 7. Nitrotoluenes, $C_7H_7 \cdot NO_2$ .

Only two of the three isomeric nitrotoluenes are used technically to any large extent.

1. *o*-Nitrotoluene, a yellowish liquid, boiling point 222° to 225°.

2. *p*-Nitrotoluene, a colourless, crystalline solid, melting point 54°, boiling point 236°.

Both isomerides are formed by the nitration of toluene; when the operation is carried out under the ordinary conditions, about 60 to 65 per cent. of the ortho- and 40 to 35 per cent. of the para-compound are obtained, the meta-compound, which is of less technical importance, being formed to the extent of 2 to 3 per cent. The separation of the mixture is effected by fractional distillation under diminished pressure.

Ortho- and para-nitrotoluene are put on the market in a state of considerable purity. The former is tested by its boiling point, and the latter by its melting point.

The estimation of *p*-nitrotoluene may be carried out by the colorimetric method proposed by Reverdin and De La Harpe.<sup>1</sup> This is based on the fact that *p*-nitrotoluenesulphonic acid, when boiled with soda, is easily converted into dinitrostilbenedisulphonic acid, which gives a red colour when dissolved in alkali, whilst the corresponding ortho-compound is not attacked by soda, and the alkaline solution is yellow. Two c.c. of pure *o*-nitrotoluene are heated on a water-bath with 6 c.c. of sulphuric acid (containing 25 per cent. of sulphur trioxide) for three hours, the product cooled and diluted to 1 litre. In a similar manner, a mixture of *o*-nitrotoluene (ninety-six parts) and *p*-nitrotoluene (four parts) is sulphonated, and the product diluted to 200 c.c. In determining the amount of *p*-nitrotoluene, the substance

<sup>1</sup> *Bull. Soc. Chim.*, 1888 [ii.], 50, 44.

and nitrotoluene (containing 4 per cent. of the para-compound) are sulphonated, the products diluted to 200 c.c., and the colours, which are obtained by mixing 1 c.c. of each solution with 5 c.c. of aqueous soda, are compared. If the sample to be analysed gives a stronger colour, a measured quantity (20 to 50 c.c.) is progressively diluted with the solution of *o*-nitrotoluenesulphonic acid until 1 c.c., when heated with 5 c.c. of aqueous soda, gives the same amount of colour as the solution containing 4 per cent. The percentage of *p*-nitrotoluene can then be calculated.

A method for the volumetric estimation of *p*-nitrotoluene in crude nitrotoluene is given by B. Glasmann.<sup>1</sup> The nitrotoluene is reduced to toluidine, and the *p*-toluidine is precipitated by a 5 per cent. ethereal solution of oxalic acid; the precipitate is washed, covered with warm water, and titrated with sodium hydroxide (modification of Rosenstiehl's method for the estimation of *p*-toluidine in the presence of *o*-toluidine. See p. 864. Cf. also Holleman's method, p. 866). *o*-Nitrotoluene is employed in the manufacture of *o*-toluidine and of toluidine. The para-compound finds application in the preparation of certain dyes.

### 8. Nitronaphthalene, $C_{10}H_7 \cdot NO_2$ .

Of the known nitro-derivatives of naphthalene only the  $\alpha$ -modification is employed technically. It is used exclusively in the manufacture of  $\alpha$ -naphthylamine. In the pure state it forms yellow prisms, melting point  $61^\circ$ , boiling point  $394^\circ$ , is insoluble in water, and dissolves easily in alcohol or ether. The technical product is tested by determining its melting point.

### 9. Dinitrobenzene, $C_6H_4(NO_2)_2$ .

Only the meta-isomeride of the dinitrobenzenes finds technical application. It is used almost exclusively in the manufacture of *m*-phenylenediamine, the intermediate product in the preparation of chrysoidine, Bismarck brown, cotton blacks, and other dyes (*e.g.*, acridine derivatives).

Pure *m*-dinitrobenzene forms long, almost colourless needles, melting point  $90^\circ$ . It dissolves easily in alcohol or ether, but not in water. The technical product consists usually of a more or less pure, yellowish crystalline cake. It should not be strongly contaminated with nitrobenzene, which is easily detected by its odour and by the lower melting point of the product, and should be neutral and give a clear solution in alcohol.

The presence of small quantities of the two isomerides of higher melting point may be neglected. Mechanically retained nitric acid is

<sup>1</sup> *Chem. Zeit.*, 1904, 28, 187; *Ber.*, 1903, 36, 4260.

frequently present. In testing it the melting point and the solidifying point are determined.

Dinitrobenzene is prepared by treating nitrobenzene with nitric and sulphuric acids at a temperature higher than that used in the case of nitrobenzene.

#### 10. Dinitrotoluene $C_7H_6(NO_2)_2$ .

The dinitrotoluene, which is obtained by the energetic treatment of toluene with nitric and sulphuric acids, consists chiefly of the asymmetric meta-compound ( $CH_3:NO_2:NO_2=1:2:4$ , melting point  $70^{\circ}.5$ ). It is used in the preparation of tolylenediamine, which, like phenylenediamine, is employed in the production of yellow, brown, and black dyes. It comes on the market in the form of a yellow cake, which should not be oily, and should be free from the odour of nitrotoluene.

#### 11. Aniline and the Toluidines.

An account of the pure bases will be given before that of the technical products.

##### (a) Aniline, $C_6H_5.NH_2$ .

Pure aniline is a colourless, oily liquid, with a peculiar odour, which slowly turns brown in the air. It solidifies in the cold to a laminated, crystalline mass melting at  $8^{\circ}$ ; its sp. gr. is 1.036 at  $0^{\circ}$ , 1.0267 at  $15^{\circ}$ , 1.0158 at  $22^{\circ}$ , and it boils at  $184^{\circ}$ . This boiling point is determined at 760 mm. and by a thermometer wholly immersed in the vapour. The boiling point is, under the usual conditions of the determination,  $181^{\circ}$  to  $183^{\circ}$ , according to the pressure. Aniline is miscible with alcohol and ether.

Water dissolves aniline to some extent when shaken with it. Conversely the aniline takes up some water. This fact is of special importance because commercial aniline is distilled with steam and separated from the condensed water; although the oil is finally distilled under diminished pressure, whereby most of the water distils first, yet it may even then contain traces of water. The mutual solubilities of aniline and water have been tabulated by Alexéeff:—

Temperature.	100 parts of water dissolve of aniline.	Temperature.	100 parts of aniline dissolve of water.
$16^{\circ}$	3.1	$8^{\circ}$	4.6
$56^{\circ}$	3.5	$25^{\circ}$	4.98
$82^{\circ}$	5.1	$39^{\circ}$	5.43
		$68^{\circ}$	6.04

When water is mixed at  $22^{\circ}$  with the necessary quantity of aniline,

a change of volume does not take place;<sup>1</sup> the amount of dissolved aniline is 3.481 volumes per 100 volumes of water, and the sp. gr. of the solution is 0.9986. On the other hand, a contraction occurs when aniline is mixed with water; 1000 c.c. of aniline and 52.22 c.c. of water occupy 1049.55 c.c. The solution of aniline has no action on red litmus paper. Aniline is, however, a well-defined base; it unites with one molecule of a monobasic acid to form well-crystallised salts. All of these have an acid reaction, even when they contain an excess of the base; the acid, therefore, can be titrated as though it were uncombined.<sup>2</sup>

Free aniline can be detected in the presence of an aniline salt by the behaviour of the former with copper sulphate. A solution of copper sulphate, quite free from acid, is coloured greenish brown by free aniline, whilst aniline salts do not give the reaction. The test, which is fairly sensitive, affords a simple means of exactly neutralising aniline with an acid.

The behaviour of free aniline with certain azo dyes, particularly Congo red (see below and Vol. I., p. 77), can also be used for its detection and acidimetric estimation. Congo red is turned blue by acids, and free aniline restores the red colour; the base can therefore be titrated with *N*-acid, using the dye as an indicator. It is best to standardise the acid against pure aniline. At the same time, any ammonia or other free alkali present can be titrated separately with litmus and allowance made for it. The results obtained by this method are not very exact, and it is always safer to titrate aniline with sodium nitrite (see p. 928).

Of the salts of aniline, the sulphate is sparingly soluble, whilst the hydrochloride dissolves fairly readily in water.

Aniline gives the following reactions:—

An aqueous (not acid) solution is coloured violet by hypochlorites (Runge's reaction).

A solution in concentrated sulphuric acid becomes at first red and then blue by the addition of a small particle of potassium bichromate (Beissenhitz's reaction).

Potassium bichromate produces in an acid solution of aniline sulphate a dark green precipitate which becomes violet-black (aniline black) by a further addition of the reagent. On heating the mixture, *p*-benzoquinone (melting point 127°) distils over. Various other characteristic colour reactions are described by Peset.<sup>3</sup>

When heated with glacial acetic acid, aniline yields acetanilide, melting at 112°.

<sup>1</sup> W. Herz, *Ber.*, 1898, 31, 2669.

<sup>2</sup> Lunge, *Dingl. polyt. J.*, 1884, 251, 40; *Chem. Ind.*, 1893, 16, 490.

<sup>3</sup> *Z. anal. Chem.*, 1909, 48, 37.

The value of all of these reactions is doubtful when aniline has to be detected in a mixture of different bases.

(b) Toluidines,  $C_7H_7.NH_2$ .

1. *o*-Toluidine.—A colourless liquid, boiling point  $198^\circ$ , sp. gr. 1.003 at  $16^\circ$ , which turns brown in the air.

Its solubility in water is similar to that of aniline. It is also a well-defined base, forming crystalline salts having an acid reaction, which show in general the behaviour of aniline salts. The hydrochloride is more easily soluble than that of aniline, but the nitrate and the picrate differ, in their sparing solubility, from the corresponding salts of aniline. The oxalate is soluble in two hundred and fifty parts of ether (distinction from *p*-toluidine and from aniline). When boiled with glacial acetic acid *o*-toluidine yields the acetyl derivative, melting at  $110^\circ$ .

An acid solution of *o*-toluidine in sulphuric acid behaves towards chromic acid like aniline, yielding a substance analogous to aniline black. By boiling the mixture, toluquinone, melting at  $67^\circ$ , is formed.

When a solution of *o*-toluidine is shaken with ether, treated drop by drop with a solution of bleaching powder, again shaken, and the ethereal layer removed and brought into contact with slightly acidified water, the latter acquires a purple-red coloration (Rosenstiehl).

An intense emerald-green colour is produced when ferric chloride is added to a faintly acidified solution of *o*-toluidine containing pure *p*-tolylenediamine (Nietzki).

2. *m*-Toluidine occurs in aniline oil only in traces, and its presence can generally be neglected. It is very similar to the preceding base, boiling at  $197^\circ$ , and having a sp. gr. of 0.998 at  $25^\circ$ ; it differs from *o*-toluidine chiefly in the lower melting point of its acetyl derivative,  $65.5^\circ$ . Other reactions have been little studied. Like *o*-toluidine, it yields toluquinone on oxidation.

3. *p*-Toluidine crystallises in colourless leaflets, melting at  $45^\circ$ , boiling at  $198^\circ$ , and having a sp. gr. of 1.046. It is slightly soluble in cold water but more readily in hot, and dissolves easily in alcohol, ether, or benzene. The base has a neutral, and the salts an acid, reaction. The hydrochloride is rather less soluble than that of *o*-toluidine or aniline. The picrate and the nitrate are more easily soluble, whilst the oxalate is characterised by its sparing solubility in water, and its almost complete insolubility in ether. When boiled with glacial acetic acid, it yields the acetyl derivative, melting at  $153^\circ$ .

When a slightly acid solution of *p*-toluidine is treated with potassium bichromate, an iridescent brown crystalline precipitate is formed, which dissolves in alcohol with a dirty violet colour. In dilute solutions a

reddish violet coloration is produced. A quinone is not formed on boiling with an excess of potassium bichromate.

A mixture of *o*-, *m*-, and *p*-toluidine is formed when toluene is nitrated, and the product reduced by iron and acetic or hydrochloric acid. Such a mixture usually contains *o*-toluidine in preponderating amount, a considerable quantity of *p*-toluidine, and only traces of *m*-toluidine. A great part of the *p*-toluidine crystallises out when the mixture is strongly cooled.

When a complete separation is desired, as, for example, in the preparation of the purest possible *o*-toluidine, the method proposed by Rosenstiehl may be used. This process depends on the fact that *p*-toluidine is a stronger base than *o*-toluidine. When sulphuric acid is added to a mixture of the two bases, in a quantity insufficient to neutralise both, the acid combines preferably with the *p*-toluidine, and by a subsequent distillation with steam a product richer in *o*-toluidine is removed. By several repetitions of the process, nearly chemically pure *o*-toluidine is obtained, whilst *p*-toluidine can be isolated, by crystallisation, from the non-volatile residues.

Another method, introduced by Friswell,<sup>1</sup> consists in mixing the oil with ice, whereby the crystalline hydrate of *p*-toluidine is formed; this is drained from the *o*-toluidine and distilled, when pure *p*-toluidine is obtained.

Pure *o*-toluidine can only be obtained by the crystallisation of its nitrate.<sup>2</sup>

The toluidines are now usually manufactured by reducing the corresponding pure nitrotoluenes, which, as already stated, are separated by distillation under diminished pressure.

### (c) Xylidines, $C_8H_9.NH_2$ .

The six isomeric xylidines which are theoretically possible are all known. Four are present in the crude xylidine which is obtained by nitrating crude xylene and reducing the resulting mixture of nitroxylenes. Only two of these, however, are present in large quantity, the amounts of the other two being negligible.

1. *m*-Xylidine ( $NH_2:CH_3:CH_3=1:2:4$ ), boiling point  $212^\circ$ , sp. gr. 0.9184 at  $25^\circ$ , constitutes 45 to 60 per cent. of commercial xylidine. The hydrochloride crystallises well and is rather sparingly soluble.

2. *p*-Xylidine ( $NH_2:CH_3:CH_3=1:2:5$ ), boiling at  $215^\circ$  under 739 mm. pressure, sp. gr. 0.980 at  $15^\circ$ , is present to the extent of 10 to 40 per cent. in commercial xylidine. When a mixture of the two bases is sulphonated with fuming sulphuric acid, the sulphonic acid of *m*-xylidine alone crystallises out on mixing with water. The base is regenerated

<sup>1</sup> *J. Soc. Chem. Ind.*, 1908, 27, 258.

<sup>2</sup> Schad, *Ber.*, 1873, 6, 1361.

by heating the sulphonic acid with hydrochloric acid under pressure. *p*-Xylidine forms an easily soluble sulphonic acid, the sodium salt of which crystallises well. The latter yields *p*-xylidine on dry distillation.<sup>1</sup>

### Technical Aniline Oils.

Technical aniline oils are prepared in the larger colour works themselves, and also in aniline works.

Although it is of the utmost importance to know the qualitative and the quantitative composition of an aniline oil, yet even now there is, in practice, an almost entire lack of trustworthy methods for the determination of all the individual constituents. In most cases the manufacturer is satisfied by the determination of the specific gravity and of the boiling point, and seeks to ascertain empirically whether the oil in question is suitable or not for the desired purpose. The determination of the boiling point will be described in some detail, as it is the most important method of ascertaining the approximate amounts, for example, of the two constituents of a mixture of aniline and toluidine. For this purpose it is by no means sufficient to determine the range of temperature within which the substance in question distils; it is more important to ascertain the quantity which passes over at a definite temperature. The most convenient apparatus is an ordinary distilling flask, placed on a sand-bath and connected to a suitable condenser: a cylinder graduated in c.c. is used as the receiver. A thermometer is placed in the neck of the flask so that the bulb is about 1 cm. below the side tube. One hundred to two hundred c.c. of the oil are distilled slowly and the distillate is collected from degree to degree in separate cylinders. The first portions are not taken into account since the thermometer will not have acquired the temperature of the vapour, and moreover they contain water. Special thermometers for the distillation of aniline are made, the scale of which begins at 150° and is divided into fifths or tenths of a degree.

The mistake must not be made of deducing the percentage content of a substance, boiling at a certain temperature, from the magnitude of the fraction which distils at this temperature. The whole estimation has only a relative value. To determine, for example, the approximate amounts of aniline and toluidine in a mixture of both, the following method must be adopted. Different mixtures, containing known quantities of the two bases, are prepared and distilled separately, and that one is noted which most nearly resembles the unknown mixture in the magnitude of the individual fractions. In so doing, it is necessary to work, as far as possible, in the same flask, with the same thermometer, and at the same pressure, and also always to distil, as nearly as possible, at the same rate (generally 100 c.c. in half an hour). After a little

<sup>1</sup> Noelting, Witt, and Forel, *Ber.*, 1885, 18, 2664.

practice, the basic mixture is soon found, the composition of which corresponds approximately with that of the oil under examination. In certain continually recurring investigations an aniline oil which fulfils the required conditions is selected as a "type," and oils which behave like the type on distillation are passed as satisfactory. In addition to the boiling point it is customary to determine the specific gravity, the value of which, however, is even more relative than that of the former. Generally the specific gravity is in the inverse ratio to the boiling point.

The contamination of aniline oils with nitrobenzene and hydrocarbons, which happens occasionally, is most easily detected by the incomplete solubility of the oils in dilute hydrochloric acid, and with still greater certainty by shaking the acid solution with ether and evaporating off the latter.

The moisture in aniline, and in *o*- and *p*-toluidine is determined by O. Dobriner and W. Schranz<sup>1</sup> by ascertaining the quantity of a bromine solution, prepared according to Reinhardt's directions (p. 860), taken up by equal weights of the undried and of the dried substance. If the undried and the dried substances require *a* and *b* c.c. respectively, the amount of moisture, *F*, is calculated from the equation:—

$$a : b = (100 - F) : 100.$$

It is immaterial whether the substances under examination are, apart from the water, pure or mixtures of aniline and toluidine; in the latter case the ratio of the constituents is the same in the dried as in the undried substance.

Aniline and *o*-toluidine are easily and completely dried by treatment, best in two operations, with ignited potassium carbonate. *p*-Toluidine, however, cannot be obtained anhydrous even by treatment with fused potassium hydroxide at about 50°; moreover, the base apparently does not remain quite unattacked under these conditions. Since commercial *p*-toluidine contains only a small quantity of aniline, it is sufficient for technical purposes to distil the *p*-toluidine and to stop the operation when 10 per cent. has passed over. The residue in the distilling vessel is regarded as anhydrous.

### Pure Aniline Oil.

Aniline oil was formerly put on the market in two qualities—namely, "Aniline for Blue" and "Aniline for Red," the former being the purest aniline obtainable, necessary for the manufacture of spirit and soluble blues, and the latter being used for the manufacture of magenta, and consisting of a mixture of aniline and the toluidines.

Now, however, pure aniline only is manufactured, and, where necessary, it is mixed with the pure *o*- and *p*-toluidines in the requisite proportions.

<sup>1</sup> *Z. anal. Chem.*, 1895, 34, 740.



The specific gravity of aniline oil varies between 1.0265 and 1.0267 at 15°. Of a good sample 95 per cent. should distil within  $\frac{1}{2}$ °. The boiling point depends on the pressure and lies between 181° and 183°. A quite clear solution should be given by 10 c.c. of the oil, 50 c.c. of water, and 40 c.c. of hydrochloric acid.

A. Liebmam and A. Studer<sup>1</sup> estimate the water and sulphur and determine the specific gravity, the boiling point, and the solubility in hydrochloric acid in the following way:—The water and the boiling point are determined in one operation. For this purpose 100 c.c. of the oil are distilled in an ordinary flask; the first 10 c.c. are collected in a narrow, graduated cylinder of 15 c.c. capacity, shaken with 1 c.c. of saturated brine, and the volume of the latter is read off. The method will not show the presence of less than 0.3 per cent. of water, consequently 0.3 c.c. must always be added to the amount of salt solution observed. The distillation is now continued and each 10 c.c. of the distillate collected. Ninety-five per cent. of the oil should distil within  $\frac{1}{2}$ °. The specific gravity of the distillate is determined, and should be 1.0265 to 1.027 at 15°.

The presence of non-basic impurities is detected by a determination of the solubility in dilute hydrochloric acid.

By boiling the oil under examination, using a reflux condenser, the sulphur is converted into hydrogen sulphide, which is estimated by driving it by a current of carbon dioxide into a standard silver solution, the excess of which is determined after filtration.

François<sup>2</sup> recommends a volumetric method for the estimation of aniline in solution, which depends on the formation of tribromoaniline. The indicator is indigotinsulphonic acid, which is decolorised when the aniline is changed completely into tribromoaniline by bromine water. The aniline can be titrated either in the free state or as the hydrochloride with an excess of hydrochloric acid, and even in the form of a solution containing about 0.01 g. of aniline per litre. The requisite bromine water must contain about 5 g. of bromine per litre; it is standardised against arsenious acid, using indigo as the indicator, or against a solution of pure aniline hydrochloride (1.392 g. per litre).

When aniline oil is heated with arsenic acid or mercuric chloride, blackish violet dyes, insoluble in water, are formed together with very small traces of rosaniline.

Aniline oil is obtained by the reduction of the purest possible nitrobenzene.

*Aniline salt* (aniline hydrochloride)\* forms large leaflets or needles, usually of a greyish or greenish grey colour, which are easily soluble in water and alcohol; it melts at 196°.5 to 196°.8 (shortened Zincke

<sup>1</sup> *J. Soc. Chem. Ind.*, 1899, 18, 110.

<sup>2</sup> *J. Pharm. Chim.*, 1899 [vi.], 9, 821.

thermometer) in a bath previously heated to  $180^{\circ}$ , and volatilises undecomposed at a higher temperature.

The solution in water should be clear, should not decolorise safrosin paper, and should give at most only a faint turbidity with a solution of barium chloride. The presence of uncombined aniline is detected by means of a solution of copper sulphate quite free from acid, which is turned greenish brown by the slightest trace of aniline (see p. 853), whilst the hydrochloride does not cause this change.

The moisture is estimated by drying 5 g. in a desiccator until the weight is constant (about twenty-four hours). At the most, the loss of weight should not exceed 1 per cent. The aniline, liberated from the aqueous solution by ammonia and dried over powdered sodium hydroxide, should distil like the best quality aniline oil.

The quality is also tested by the melting point, and by titration. For the latter purpose a weighed quantity is dissolved in water and treated with  $N/10$  sodium hydroxide until a faint red coloration is produced, phenolphthalein being used as the indicator.

Reinhardt's method (below) can also be employed for the examination of the salts of aniline (and of the toluidines). The estimation must be performed on the anhydrous substance, dried over sulphuric acid.

For aniline salt Reinhardt's equation becomes:—

$$X = 2.5102VT - 1.5102A$$

where A = the amount of aniline salt taken

X = the amount of aniline hydrochloride therein

T = the titre of the brominating liquor determined by means of pure aniline hydrochloride, and also by multiplying the aniline titre by 129.5/93

V = the number of c.c. of the brominating liquor used.

To estimate the free acid, a solution of 5 g. of aniline salt in 10 c.c. of water is treated with five drops of a solution of crystal violet (1:1000), and compared with an exactly similarly prepared solution of the pure hydrochloride; the solution is titrated with a  $N/10$  aqueous solution of aniline until the colour of both solutions is the same.<sup>1</sup>

Aniline salt is employed in large quantities in the manufacture of aniline black and in the preparation of diphenylamine, etc.

### Estimation of Aniline and the Toluidines and their Mixtures.

Reinhardt's method for the analysis of aniline oils,<sup>2</sup> the underlying principle of which has been stated by A. Winther,<sup>3</sup> depends on the facts that (1) by treatment in dilute acid solution with a mixture of potassium bromide and bromate, aniline yields tribromoaniline, whilst

<sup>1</sup> A. Liebmann and A. Studer, *J. Soc. Chem. Ind.*, 1899, 18, 110.

<sup>2</sup> *Chem. Zeit.*, 1893, 17, 413.

<sup>3</sup> *Chem. Ind.*, 1905, 28, 29.

*o*- and *p*-toluidine give only dibrominated substitution products; (2) under definite conditions, oxalic acid precipitates from a solution of the three bases in hydrochloric acid, first *p*-toluidine and then aniline, whilst *o*-toluidine remains in the solution.

By titration with the brominating solution, the ratio of aniline to *p*-toluidine is determined in the oils regenerated from the separated oxalates.

**I. Estimation of Aniline, *o*-Toluidine, and *p*-Toluidine, and also of Aniline mixed with *o*- or *p*-Toluidine or with both.**—The brominating liquor is prepared from 490 g. of bromine, 336 g. of potassium hydroxide (100 per cent.), and 1 litre of water; after being boiled moderately for two to three hours the solution is diluted to 9 litres. Potassium hypobromite must not be present.

For the standardisation and also in analyses, 1.5 to 2 g. of the oil are dissolved in 100 c.c. of hydrobromic acid, sp. gr. 1.45 to 1.48 (or the equivalent quantities of potassium bromide and hydrochloric acid), and 1000 c.c. of distilled water, and titrated with the brominating liquor until potassium iodide-starch paper indicates the presence of an excess of bromine.

The titre of the brominating liquor remains fairly constant.

The aniline content of technical aniline oils is calculated from the equations:—

$$x = 2.3777vt - 1.3777a, \text{ and } p \text{ per cent.} = \frac{100x}{a},$$

where  $x$  is the amount of aniline contained in  $a$ , the amount of the oil taken,  $v$  is the volume of brominating liquor used, and  $t$  is the aniline titre of the brominating liquor;  $a - x$  represents, therefore, the amount of the toluidines in the aniline oil.

**II. Estimation of *p*-Toluidine in Mixtures with Aniline or *o*-Toluidine or both Bases.**—In order to obtain an accurate result, the quantity of oxalic acid must be more than equivalent to the *p*-toluidine present. On this account the amount of the latter is determined approximately in a preliminary experiment. The best plan, when 100 g. of oil are used in the analysis, is to increase the quantity of *p*-toluidine, found in the preliminary experiment, by 10 g. in the case of oils poor in aniline, and by 20 g. when the oil contains a large amount of aniline, and to calculate the quantity of oxalic acid accordingly. In other respects the analysis is performed in the following way:—One hundred g. of the oil are mixed with 106 g. of hydrochloric acid (sp. gr. 1.16, about 31 per cent. HCl, equivalent = 116) as free as possible from sulphuric acid, and the mixture is treated at once with the previously prepared, almost boiling solution of the requisite amount of oxalic acid, free from lime, in ten times the quantity of distilled water. The solution must remain quite clear at first, even

when a large amount of *p*-toluidine is present; it is frequently stirred while cooling and left for forty-eight hours to crystallise. The oxalates are then collected at the pump, washed thrice with 25 c.c. of distilled water, and decomposed by adding them to a hot, dilute solution of potassium hydroxide (100 c.c. of a solution of potassium hydroxide sp. gr. 1.45, and 200 c.c. of distilled water). The liberated oil, when cold, is collected and weighed. Finally, it is dried with potassium hydroxide, and the amount of aniline is estimated by titration with bromine by the method already described. A simple calculation gives the amount of *p*-toluidine in the original mixture, to which must be added a constant correction of 2.00, ascertained for the given conditions.

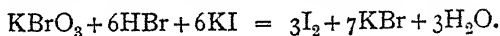
*Estimation of Aniline in the presence of a small quantity of Toluidine, and Estimation of Toluidine in the presence of a small quantity of Aniline.*<sup>1</sup>—The detection and estimation of a small quantity of toluidine in aniline are possible by Reinhardt's method (according to Dobriner and Schranz) but the results are not quite accurate when toluidine is titrated alone or mixed with a small quantity of aniline. If the aniline titre of the brominating liquor is used, aniline is found in pure toluidine, and the percentage of aniline, in mixtures of toluidine and small quantities of aniline, is too high. In the titration of pure toluidine, the result is about 10 per cent. too high when a toluidine titre, calculated from the aniline titre, is employed. Reinhardt's formula gives satisfactory results, however, when the standardisation of the brominating solution is effected against pure toluidine and the aniline titre is calculated by multiplying by  $\frac{93}{160.5}$ .

It is usually advisable to standardise the solution against pure aniline and also against pure toluidine. If *t* and *T* are the respective titres, the amount of aniline, *x*, is given by the equation:—

$$\frac{x}{t} + \frac{x-a}{T} = V.$$

Schaposchnikoff and Sachnowsky<sup>2</sup> state that Reinhardt's method is not free from objections; in particular, the preparation of the brominating solution (by boiling bromine with aqueous potassium hydroxide) gives varying and untrustworthy results.

A safer method is to employ commercial, pure potassium bromate (8 g. of potassium bromate per litre = about *N*/7, instead of 11.1 per litre, according to Reinhardt). The aniline oil is dissolved in 25 per cent. hydrobromic acid in the proportion of 60 g. of acid to 1 g. of aniline; the solution of potassium bromate is standardised, not with aniline, but with iodine, according to the equation:—



<sup>1</sup> P. Dobriner and W. Schranz, *Z. anal. Chem.*, 1895, 34, 734.

<sup>2</sup> *Z. Farb. Ind.*, 1903, 2, 7.

For the standardisation, 25 c.c. of the solution of potassium bromate are treated with 5 g. of potassium iodide and 3 c.c. of 25 per cent. hydrobromic acid. The liberated iodine is titrated with standard sodium thiosulphate. Three molecules of iodine correspond with 1 molecule of potassium bromate, 1 molecule of aniline, or 1.5 molecules of toluidine. The numerical proportions are :—

$$\begin{aligned} 1 \text{ g. of iodine} &= 0.22083 \text{ g. of potassium bromate,} \\ &= 0.12231 \text{ g. of aniline,} \\ &= 0.14061 \text{ g. of toluidine.} \end{aligned}$$

*Example.*—Twenty-five c.c. of the potassium bromate solution required 72.6 c.c. of standard sodium thiosulphate (1 c.c. = 0.01147 g. of iodine).

Hence—

$$\begin{aligned} 1 \text{ c.c. of the potassium bromate solution} &= 0.0332 \text{ g. of iodine,} \\ &= 0.00407 \text{ g. of aniline,} \\ &= 0.00468 \text{ g. of toluidine.} \end{aligned}$$

*Control Experiment.*—Dissolve 5.0318 g. of pure aniline in 187.5 g. of 40 per cent. hydrobromic acid, and dilute the solution with water to 500 c.c. Twenty-five c.c. of the solution required 61.8 c.c. of the potassium bromate solution; the total quantity will require 1236 c.c. Therefore the aniline titre of the potassium bromate solution = 0.00407 g. of aniline.

Potassium iodide-starch paper is unnecessary for the detection of the end-point; when bromination is complete, the liquid above the brominated precipitate is quite clear and assumes an easily visible yellowish colour on the addition of the slightest excess of potassium bromate. This coloration indicates the end of the reaction very sharply. The amounts of aniline and of toluidine in the oil under examination are calculated from the results of the analysis by the following formulæ :—

If  $p$  = the weight of aniline oil taken

$n$  = number of c.c. of the solution of potassium bromate corresponding with  $a$  g. of the oil

$T_i$  = iodine titre of the solution of potassium bromate

$T_a$  = aniline titre of the solution of potassium bromate

$$= 0.12231 \times T_i$$

$T_t$  = toluidine titre of the solution of potassium bromate

$$= 0.14061 \times T_i$$

the percentage of aniline is given by

$$X_a = T_a \cdot \frac{100}{p} \cdot \frac{nT_i - p}{T_i - T_a}$$

and the percentage of toluidine by

$$X_t = T_t \cdot \frac{100}{p} \cdot \frac{p - nT_a}{T_i - T_a}$$

The oil under examination consists of pure aniline when  $n_{\text{D}}^{20} = p$ , and of pure toluidine when  $n_{\text{D}}^{20} = a$ .

**Magenta "échappés."**—Aniline oils recovered from the magenta fusion by distillation consist mainly of aniline and *o*-toluidine, whilst the *p*-toluidine is utilised almost completely in the formation of magenta. They are employed chiefly in the manufacture of safranine. Most magenta "échappés" behave like a mixture of 40 per cent. of aniline and 60 per cent. of *o*-toluidine. They always contain a considerable quantity of non-basic products, and give, therefore, a turbidity with dilute hydrochloric acid.

**Technical Toluidines.**—Commercial *p*-toluidine can easily be judged by its appearance, as well as by its melting point. It forms a hydrate, and special attention must be given to this fact. *o*-Toluidine is also placed on the market in a state of great purity. Special attention is paid to the specific gravity, since *o*- and *p*-toluidines differ considerably from one another in this property, but not in their boiling points.

The table on p. 864, prepared by Lunge, gives the specific gravities of mixtures of the two bases, and suffices for their quantitative examination, provided they are dry and quite free from aniline and xylydine. Such a toluidine mixture must distil entirely between 195° and 198°, the main portion within 2°.

When a solution of *o*-toluidine in dilute hydrochloric acid is treated with potassium bichromate and a drop of the mixture is placed on filter paper, the presence of *p*-toluidine is detected by a reddish violet rim surrounding the stain.

*A Colour Reaction of p-Toluidine*,<sup>1</sup> which can be used for the detection of the base, alone or mixed with aniline and its homologues, depends on the different behaviour of the bases towards ferric chloride. When a cold, faintly acid solution of *p*-toluidine in hydrochloric acid is treated with a few drops of ferric chloride, it remains light yellow at first, becoming rose-red, however, after some time. If it is heated to boiling and then cooled, it acquires at once an intense Bordeaux red colour, which is very stable and does not change after a day's keeping. It is still distinctly perceptible when 1 g. of *p*-toluidine is dissolved in about 3 litres of water, slightly acidified with hydrochloric acid; at still greater dilutions the red colour is masked by the yellow colour of the ferric chloride, thus making the detection of the *p*-toluidine uncertain. An aqueous solution of *o*-toluidine hydrochloride yields with ferric chloride, after keeping for a short time, a blue precipitate, which becomes greenish with more hydrochloric acid (toluidine blue)<sup>2</sup>;

<sup>1</sup> J. Biehringer and A. Busch, *Chem. Zeit.*, 1902, 26, 1123.

<sup>2</sup> A. Ladenburg, *Ber.*, 1877, 10, 1127.

on boiling, the precipitate is formed immediately, and is blue or greenish blue according to the acidity of the solution.

**Compositions of Mixtures of *o*- and *p*-Toluidines determined by the Specific Gravities (Lunge<sup>1</sup>).**

(a) at 15°, referred to water at 15°.

Spec. Grav.	Per cent. <i>o</i> -Toluidine.	Spec. Grav.	Per cent. <i>o</i> -Toluidine.	Spec. Grav.	Per cent. <i>o</i> -Toluidine.
1·0037	100	1·0015	82	0·9993	64
1·0036	99	1·0014	81	0·9992	63
1·0035	98	1·0013	80	0·9991	62
1·0034	97	1·0012	79½	0·9990	61½
1·0033	96	1·0011	78½	0·9989	61
1·0032	95	1·0010	77½	0·9988	60
1·0031	94	1·0009	77	0·9987	59
1·0030	93½	1·0008	76	0·9986	58½
1·0029	92½	1·0007	75	0·9985	58
1·0028	91½	1·0006	74	0·9984	57½
1·0027	91	1·0005	73	0·9983	56½
1·0026	90	1·0004	72½	0·9982	56
1·0025	89½	1·0003	72	0·9981	55
1·0024	88½	1·0002	71	0·9980	54½
1·0023	88	1·0001	70	0·9979	54
1·0022	87	1·0000	69	0·9978	53
1·0021	86½	0·9999	68½	0·9977	52½
1·0020	86	0·9998	68	0·9976	51½
1·0019	85	0·9997	67	0·9975	51
1·0018	84½	0·9996	66½	0·9974	50
1·0017	83½	0·9995	65½		
1·0016	82½	0·9994	65		
(b) at 20°, referred to water at 15°.					
0·9939	50	0·9934	46½	0·9929	43
0·9938	49½	0·9933	46	0·9928	42
0·9937	48½	0·9932	45	0·9927	41
0·9936	48	0·9931	44½	0·9926	40
0·9935	47½	0·9930	44		

The different behaviour of the two isomerides furnishes a means for their detection, for example, in commercial toluidine. When a faintly acid solution of this in hydrochloric acid is heated with a few drops of ferric chloride, a blue-green flocculent precipitate is obtained (due to *o*-toluidine); the filtrate shows the cherry-red coloration indicative of *p*-toluidine.

Pure aniline also gives a blue-green precipitate under analogous conditions. A mixture of aniline and *p*-toluidine exhibits, therefore, the same behaviour as the mixture of the two toluidines.

For the estimation of *p*-toluidine in the presence of *o*-toluidine, Rosenstiehl has proposed a method, which depends on the different

<sup>1</sup> *Chem. Ind.*, 1885, 8, 74.

solubilities of the oxalates in ether. As the first step in the estimation, ether is prepared completely free from alcohol by washing it repeatedly with water, drying it over calcium chloride, and finally distilling it from sodium. About 3 g. of crystallised oxalic acid are dissolved in 1 litre of the ether. Then 0.2 to 0.4 g. of pure *p*-toluidine is weighed out accurately and dissolved in 80 to 100 c.c. of the ether in a flask, and the ethereal solution of oxalic acid is run in from a burette as long as a precipitate is formed. The correct determination of the end-point causes some trouble, because, towards the end of the estimation, the precipitate appears only after shaking for some time, and is then deposited on the walls of the vessel. Finally, a small portion must be filtered into a test tube and examined to find out whether a drop of the solution of oxalic acid still gives a turbidity after some shaking and when the walls of the vessel are rubbed. When the end-point has been determined, the titre of the solution of oxalic acid is easily calculated. The substance under examination is then treated exactly like the *p*-toluidine, and the amount of this base is calculated from the volume of the solution of oxalic acid employed.

Lorenz modifies the method, in that he treats the solution with a slight excess of oxalic acid, filters, washes the precipitate thoroughly with ether, dissolves it in *N*/10 sodium hydroxide, and titrates the excess of the alkali with *N*/10 acid. Since oxalic acid in combination with toluidine acts on litmus like a free acid, the amount of oxalic acid in the precipitate can be estimated with satisfactory accuracy. The amount of *p*-toluidine is then easily calculated from the formula of toluidine oxalate  $(C_7H_9N)_2C_2H_2O_4$ .

Rosenstiehl's method gives tolerably accurate results, provided that ether, absolutely free from alcohol, is used, and such is obtained only by keeping it over sodium for a week. If the ether contains a trace of alcohol, the solution of oxalic acid produces no precipitate whatever in a mixture which contains less than 5 per cent. of *p*-toluidine.

Häussermann<sup>1</sup> proposes the following method for the estimation of small quantities of *p*-toluidine in *o*-toluidine.

A solution of 88 g. of crystallised oxalic acid in 750 c.c. of water and 43 c.c. of hydrochloric acid (sp. gr. 1.18) is heated at 70° to 75° in a porcelain basin, and is treated with 10 g. of the toluidine; the mixture is warmed and stirred until any undissolved oxalate has completely passed into solution, and is then allowed to cool slowly, with occasional agitation of the liquid, until a just perceptible separation of oxalate is noticeable on the surface, which takes place at 30° to 35°. As soon as a small quantity has crystallised and a pause in the crystallisation ensues (for example, after the separation of 0.5 g.), the liquid is filtered rapidly through coarse linen, and the crystals are washed with a few drops of

<sup>1</sup> *Chem. Ind.*, 1887, 10, 55.



water and gently pressed. If this first mass of crystals has a smooth, white, lustreless appearance, the filtration is repeated after a short time, when a further separation of crystals, approximately equal to the first, is obtained. The collection of the separate fractions is continued until crystalline scales are no longer formed, but a highly lustrous crystalline mass, which consists of pure *o*-toluidine oxalate and is easily distinguishable from the first crystals, which contain *p*-toluidine oxalate. When this point is reached, the liquid is quite free from *p*-toluidine.

The individual crystalline fractions are distilled in turn with a solution of sodium carbonate, and the base which passes over with the steam is next qualitatively tested by cooling it by ice. If the sample becomes solid merely by stirring, the mass is collected on a tared filter, gently pressed, dried over sodium hydroxide, and weighed as *p*-toluidine. If the mass solidifies only after inoculation with a crystal of pure *p*-toluidine, only the half of its weight is regarded as *p*-toluidine. When the base from the first crystalline fraction remains liquid under these conditions, the toluidine under examination can be regarded, for technical purposes, as free from the para-isomeride. From a commercial *o*-toluidine of good quality it is necessary, as a rule, to collect and distil only two fractions of 0.3 to 0.5 g., the oil obtained from the second fraction usually remaining liquid.

The quantities stated above are applicable only for products which do not contain more than 8 to 10 per cent. of *p*-toluidine. When a sample containing a greater percentage has to be examined it must be previously diluted with pure *o*-toluidine; conversely, in the examination of a product containing only a trace of *p*-toluidine, the main portion of the ortho-isomeride is separated as the picrate, which is sparingly soluble in alcohol, from a large quantity of the toluidine, whilst the residual picrates, which remain dissolved in the cold alcohol, are reconverted into a mixture of the two bases, which is then treated by the method described above.

A very good method of estimating small amounts of *p*-toluidine in *o*-toluidine is Schoen's colorimetric method. A standard oil is prepared containing 8 per cent. of *p*-toluidine and 92 per cent. of *o*-toluidine, 1 c.c. of which is dissolved with 2 c.c. of pure hydrochloric acid in 50 c.c. of water, and oxidised cold by adding 1 c.c. of a saturated solution of potassium bichromate. After standing for two hours, the product is filtered, the precipitate being washed with water, and the filtrate and washings made up to 100 c.c. The toluidine to be tested is treated in the same manner, and compared colorimetrically with the above solution. Another method, described by A. F. Holleman,<sup>1</sup> consists in converting the sample into the acetyl derivative and observing the

<sup>1</sup> *Proc. K. Akad. Wetensch. Amsterdam*, 1904, 7, 395; *Rec. trav. chim.*, 1908, 27, 458.

solidifying point. The solidifying points of known mixtures of the acetyl compounds of *o*- and *p*-toluidine are given in the following table:—

Percentage of <i>p</i> -compound.	Solidifying point ° C.
0	109·15
1·12	108·45
2·42	107·75
9·58	103·2
13·6	100·8

42·8 g. of the toluidine to be tested are added slowly to a solution of 25·2 g. of oxalic acid dissolved in 1 litre of hot water. After cooling to 0°, the crystals are collected on a filter and washed once with a little water. The toluidine is then regenerated from both crystals and filtrate by adding sodium hydroxide and distilling in steam. After separating the oil, the aqueous liquor must be extracted twice with ether to avoid loss. Both portions of toluidine are now converted into the acetyl compound by using, for 1 g. of toluidine, 2 c.c. of glacial acetic acid and 1 c.c. of acetic anhydride, evaporating on a water-bath, and distilling in a vacuum. The solidifying point of the two portions is determined and the amount of *p*-toluidine deduced from the above table. When the amount of *p*-compound exceeds 1 to 2 per cent., the toluidine can be directly converted into the acetyl derivative without first preparing the oxalate.

This method may be used also for detecting the presence of *p*-nitrotoluene in *o*-nitrotoluene by first reducing with iron and hydrochloric acid and treating the resulting toluidine in the above manner.

## 12. Xylidine.

Xylidine is employed in large quantities in the preparation of azo dyes. As has been mentioned previously, the commercial product is a mixture which contains chiefly asymmetrical *m*-xylidine together with a smaller quantity of *p*-xylidine. The former, being suitable principally for the preparation of azo dyes, is frequently separated in the form of its sparingly soluble hydrochloride; a complete separation from the para-isomeride is, however, not possible by this means.

A satisfactory separation can be effected by means of glacial acetic acid. To 121 parts of crude xylidine are added 30 parts of glacial acetic acid, and the mixture allowed to stand for some weeks. When crystals of *m*-xylidine acetate have separated out, these are collected (best by means of a centrifugal machine), and basified with sodium hydroxide. The filtrate from the *m*-xylidine acetate contains the

*p*-xylydine, which may be separated as hydrochloride by adding hydrochloric acid.<sup>1</sup>

Commercial xylydine boils generally between 210° and 220°, and has a sp. gr. of 0.9815 and 0.9840. Its solution in dilute hydrochloric acid should be as clear as is possible. In most cases its suitability must be decided by the quality of the resulting azo dyes.

### 13. Pseudocumidine.

This asymmetrical aminotrimethylbenzene finds application in the preparation of red azo dyes, and is obtained by heating *as-m*-xylydine, methyl alcohol, and hydrochloric acid to a high temperature (280° to 290°). The pure crystalline base melts at 63° and boils at 235°—236°. The nitrate is sparingly soluble.

### 14. Methylanilines.

The products obtained by methylating aniline are employed, to a great extent, in the manufacture of violet, green, and other dyes. Dimethylaniline is used to by far the greatest extent, and its preparation and examination are of the utmost importance in the colour industry, whilst methylaniline is of less consequence.

(a) *Methylaniline*,  $C_6H_5.NH.CH_3$ , in the pure state, is an oily liquid which has a sp. gr. 0.976 at 15° and boils at 190°—191°. It is a weak base, and with acids yields salts which are easily soluble and difficultly crystallisable. In contact with acetic anhydride it develops much heat and forms an acetyl derivative, melting at 100°. On the addition of sodium nitrite or potassium nitrite to a solution of methylaniline in an excess of dilute hydrochloric acid nitrosomethylaniline is obtained as a greenish yellow oil, which is insoluble in acids and is reconverted into methylaniline by reducing agents.

Methylaniline is employed only occasionally in the preparation of violet dyes; nevertheless, its detection is of great importance because it frequently occurs as an undesirable impurity in technical dimethylaniline. It is manufactured by heating equal molecular quantities of aniline hydrochloride and methyl alcohol at 200°. The resulting crude product usually contains aniline and dimethylaniline, of which the former is removed as aniline sulphate by the addition of dilute sulphuric acid, whilst the latter is usually neglected.

(b) *Dimethylaniline*,  $C_6H_5.N(CH_3)_2$ , in the pure state, is an oily liquid with a characteristic, unpleasant odour; it boils at 192°, and has a sp. gr. of 0.9553 at 15°. It solidifies in the cold to a crystalline mass which melts at 0.5°. It is a weak base and its salts crystallise with

<sup>1</sup> Hodgkinson and Limpach, *J. Chem. Soc.*, 1900, 77, 65.

difficulty. A reaction and an increase of the temperature do not take place when it is mixed with acetic anhydride.

Dimethylaniline is used in the preparation of methyl violet, crystal violet, auramine, malachite green, etc., and is therefore one of the most important materials employed in the colour industry. It is manufactured by heating aniline with methyl alcohol and a little sulphuric acid in an autoclave to  $230^{\circ}$ — $235^{\circ}$ .<sup>1</sup>

Its faintly acidified solution yields a violet dye (methyl violet) with copper salts and potassium chlorate. Its solution in hydrochloric acid is coloured yellow by sodium nitrite without becoming turbid, but if sufficiently concentrated deposits yellowish green crystals of nitroso-dimethylaniline hydrochloride. When the latter is warmed, reduced by hydrogen sulphide, and treated, in the presence of an excess of this reagent, with ferric chloride, a fine blue dye (methylene blue) is obtained. The determination of the boiling point alone, although always to be observed, does not suffice for the examination of dimethylaniline, since it differs but slightly from methylaniline in this respect.

The impurities in dimethylaniline which require special mention are aniline, methylaniline, methyltoluidine (produced by intramolecular change when the temperature is too high), and also higher condensation products originating from impurities in the wood spirit. The last are detected by the increase in the boiling point.

Aniline can be removed, as the crystalline sulphate, by the addition of dilute sulphuric acid.

Methylaniline is almost always a constant impurity, the quantity of which varies from 0.5 to 5 per cent. or more. For the detection of methylaniline and dimethylaniline in presence of each other, Emde's method<sup>2</sup> may be used. It depends on the fact that their platinichlorides can be fractionally crystallised from an alcoholic solution.

A very convenient method has been given by Boasson and Noelting for the estimation of this base, which is very important. It depends on the above-mentioned different behaviour of the secondary and the tertiary bases towards nitrous acid. The former yield non-basic nitrosoamines which are soluble in ether, whilst in the latter the nitroso group enters the benzene nucleus. The resulting nitroso-derivatives have basic properties, and form salts which are insoluble in ether, and are therefore easily separable from the nitrosoamines.

Although this behaviour can be utilised for the estimation of the two bases in the presence of one another, a method is generally used for this purpose, which is much simpler and more rapid. It depends on the facts that methylaniline and acetic anhydride interact with an

<sup>1</sup> Walther, *Chem. Zeit.*, 1910, 34, 641, 667, 681, 690, 701.

<sup>2</sup> *Arch. Pharm.*, 1909, 247, 77.

evolution of heat, and that the consequent increase of temperature is an approximate measure of the amount of this base.

For the estimation, every 5 c.c. of the dimethylaniline under examination is mixed with 5 c.c. of acetic anhydride, both substances being initially at atmospheric temperature. About 0.5 per cent. of methylaniline is estimated for each 1° rise of temperature. It is noteworthy that the temperature of absolutely pure dimethylaniline is lowered by about 0.5° by the addition of acetic anhydride, and an allowance must be made for this behaviour in the preceding calculation.

Reverdin and de la Harpe<sup>1</sup> recommend the following method for the estimation of the constituents of a mixture of aniline, methylaniline, and dimethylaniline.

*Estimation of the Aniline.*—A solution of 7 to 8 g. of the mixture in 28 to 30 c.c. of hydrochloric acid is diluted to 100 c.c. with water. A standard solution of R-salt (sodium naphthol-3:6-disulphonate) is also prepared, containing per litre a quantity of the reagent equivalent to about 10 g. of naphthol.

To 10 c.c. of the solution of the bases, diluted with water and ice, is added, for the purpose of diazotisation, as much sodium nitrite as though aniline alone were present, and the mixture is poured gradually into a known volume of the solution of R-salt, to which an excess of sodium carbonate has been added. The resulting dye is precipitated by sodium chloride and removed, and the filtrate is tested for an excess of diazonium salt or of R-salt, by the addition of one or other of these substances. By repeated trials the volume of the solution of R-salt is determined, which is necessary to react with the diazonium salt contained in the 10 c.c. of the solution of the basic mixture.

Too much aniline is usually found in oils which contain a large percentage of aniline. This is chiefly due to the fact that the sodium chloride, employed to precipitate the dye, also salts out sodium 2-naphthol-3:6-disulphonate. The filtrate contains, therefore, less R-salt than has been actually utilised, and consequently the percentage of aniline is calculated too high.<sup>2</sup> Cf., however, p. 888.

*Estimation of the Methylaniline.*—One to two g. of the mixture to be analysed are weighed into a flask, which can be connected to a reflux condenser and heated on the water-bath, and a known quantity of acetic anhydride, corresponding with about twice the weight of the mixture, is added as rapidly as possible (for greater convenience the acetic anhydride is contained in a dropping-funnel which is weighed before and after the addition of the anhydride, so that the amount used is accurately known). The flask is connected to the condenser and the

<sup>1</sup> Ber., 1889, 22, 1004.

<sup>2</sup> Vaubel, Chem. Zeit., 1893, 17, 465.

reaction is allowed to proceed for about half an hour at the ordinary temperature. About 50 c.c. of water are then added and the mixture is heated on the water-bath for three-quarters of an hour, whereby the excess of acetic anhydride is decomposed completely. After being cooled the liquid is made up to a known volume and the acetic acid therein is titrated by standard sodium hydroxide. Phenolphthalein is used as the indicator. The amount of methylaniline is then calculated from the quantity of acetic anhydride utilised, of course after subtracting the amount of the latter which has been consumed in acetylating the aniline contained in the mixture. •

The method is correct in principle, and the sample analyses worked out by Reverdin and de la Harpe are concordant. In view of the purity which is claimed for commercial dimethylaniline at the present time, an accurate quantitative analysis should be but seldom necessary, since the thermochemical method, cited above, gives sufficient information whether a dimethylaniline is suitable or must be rejected.

O. Hinsberg and J. Kessler<sup>1</sup> recommend the benzenesulphonyl chloride method for the separation of primary and secondary bases.

### 15. Ethylaniline.

Ethylaniline is the chief product when aniline hydrochloride is heated with ethyl alcohol. Diethylaniline is obtained only by the repeated treatment of this base with ethyl chloride or bromide.

(a) *Ethylaniline*,  $C_6H_5 \cdot NH \cdot C_2H_5$ , is a colourless liquid, boiling point  $204^\circ$ , sp. gr. 0.954 at  $18^\circ$ . It is converted into an oily nitrosoamine by nitrous acid and into an acetyl derivative by acetic anhydride.

(b) *Diethylaniline*,  $C_6H_5 \cdot N(C_2H_5)_2$ , boiling point  $213.5^\circ$ , sp. gr. 0.939 at  $18^\circ$ , is a colourless liquid.

The determination of the boiling point and the specific gravity on the one hand, and the behaviour towards acetic anhydride on the other, suffice for its examination.

Here again the amount of ethylaniline can be determined from the rise of temperature produced by the addition of acetic anhydride. Vaubel<sup>2</sup> recommends the following method:—The amount of aniline is first ascertained by R-salt, according to Reverdin and de la Harpe's method (p. 870). A mixture of 25 c.c. of the oil under examination and 50 c.c. of xylene is treated with 25 c.c. of acetic anhydride at the same temperature. A cooling effect is produced when the oil is mixed with the xylene, and of course time must be allowed for the readjustment of the temperature before the anhydride is added. From the accurately measured increase of temperature an amount is subtracted equal to the increase which would be observed in a mixture of diethyl-

<sup>1</sup> *Ber.*, 1905, 38, 906.

<sup>2</sup> *Chem. Zeit.*, 1893, 17, 466.

aniline and aniline (total volume 25 c.c.) containing as much aniline as has been found in the oil under examination. For example, if 8 per cent. of aniline has been found, the increase of temperature observed in a mixture of 2 c.c. ( $=\frac{8}{4}$ ) of aniline and 23 c.c. ( $=\frac{20}{4}$ ) of diethylaniline is  $7^{\circ}5$ . The remainder of the increase of temperature is due to methylaniline, the amount of which is easily calculated, by interpolation, from the following tables:—

## I.

Total mixture			Acetic Anhydride.	Temperature increase.	Difference.	Difference for every 4 per cent. of Ethylaniline.
Xylene.	Ethylaniline.	Diethylaniline.				
c.c.	c.c.	c.c.	c.c.	° C.		
50	25	0	25	68.3		
50	24	1	25	65.2	3.1	3.1
50	23	2	25	62.7	2.5	2.5
50	22	3	25	59.6	3.1	3.1
50	21	4	25	56.7	2.9	2.9
50	20	5	25	54.2	2.5	2.5
50	19	6	25	51.5	2.7	2.7
50	18	7	25	48.8	2.7	2.7
50	15	10	25	41.8	7.5	7.5
50	10	15	25	26.9	14.4	2.9
50	5	20	25	12.4	14.5	2.9
50	4	21	25	9.4	3.0	3.0
50	3	22	25	6.3	3.1	3.1
50	2	23	25	3.3	3.0	3.0
				increases slowly	3.1	3.1
50	1	24	25	40.3		
50	0	25	25	-2.9	3.2	3.2

## II.

Total mixture			Acetic Anhydride.	Temperature increase.	Difference.	Difference for every 4 per cent. of Aniline.
Xylene.	Aniline.	Diethylaniline.				
c.c.	c.c.	c.c.	c.c.	° C.		
50	25	0	25	93.5		
50	24	1	25	94.8	3.7	3.7
50	20	5	25	86.5	8.3	2.1
50	15	10	25	67.0	19.5	3.9
50	10	15	25	44.6	22.4	4.5
50	5	20	25	21.8	22.8	4.6
50	4	21	25	17.0	4.8	4.8
50	3	22	25	12.5	4.5	4.5
50	2	23	25	7.5	5.0	5.0
50	1	24	25	2.4	5.1	5.1
50	0	25	25	-2.9	5.3	5.3

Diethylaniline is employed in the preparation of brilliant green, ethyl violet, etc.

**16. Diphenylamine,  $(C_6H_5)_2NH$ .**

Pure diphenylamine forms colourless leaflets with a peculiar odour, melting at  $54^\circ$ , and boiling at  $310^\circ$ . It is a very weak base, and its salts are decomposed even by water. It is almost insoluble in water, but dissolves readily in alcohol, ether, or benzene. When warmed with acetic anhydride it forms an acetyl derivative, melting at  $103^\circ$ . Nitrous acid converts it into a nitrosoamine. It reacts vigorously with fuming nitric acid, yielding hexanitrodiphenylamine. When heated with oxalic acid or hexachloroethane, it forms a magnificent blue dye (diphenylamine blue). With sulphuric acid containing nitric acid, it also develops a fine blue coloration.

It is employed technically for the preparation of Helvetia blue, of orange-yellow azo dyes, and of hexanitrodiphenylamine.

Commercial diphenylamine should be fairly colourless, and have the correct melting point; it should not be greasy, or possess an unpleasant odour, or turn brown in the air. When powdered and shaken with a solution of bleaching powder, it ought not to produce a violet coloration (due to aniline). For its quantitative estimation an alcoholic solution is slowly treated with an excess of bromine in alcohol until no further precipitate of the tetrabromo-derivative is produced. About twice the volume of water is added with stirring, and the mixture heated until the alcohol and excess of bromine are removed, and the precipitate becomes granulated; this is collected in a tared Gooch crucible, washed with warm water, and dried at  $98^\circ$ — $100^\circ$ .<sup>1</sup> Diphenylamine is prepared by heating aniline hydrochloride and aniline at  $230^\circ$  under pressure.

**17. Methyldiphenylamine,  $(C_6H_5)_2N \cdot CH_3$ .**

This feeble base is a viscous liquid, boiling at  $282^\circ$ . Its salts are decomposed very easily by water. It is coloured violet by a mixture of sulphuric and nitric acids. Oxalic acid and hexachloroethane convert it, like diphenylamine, into blue dyes. Methyldiphenylamine is prepared by heating diphenylamine hydrochloride with methyl alcohol in closed vessels at  $250^\circ$  to  $300^\circ$ .

**18. Naphthylamines,  $C_{10}H_7 \cdot NH_2$ .**

I.  *$\alpha$ -Naphthylamine*, in the pure state, crystallises in colourless leaflets, which melt at  $50^\circ$  and possess a very unpleasant odour. It sublimes easily and boils at  $300^\circ$ . It dissolves sparingly in water,

<sup>1</sup> Dreger, *Z. ges. Schiess-Sprengstoffwesen*, 1909, 4, 123.



easily in alcohol or ether. It turns a dirty pink in the air—less rapidly, however, when pure than when impure. Being a moderately strong base, it reacts with acids to form salts, which crystallise well. The salts are much less soluble than those of the benzenoid bases. By treatment with glacial acetic acid, it forms an acetyl derivative, melting at 159°. Commercial  $\alpha$ -naphthylamine occurs in almost colourless masses, which have at most a superficial pinkish colour.

It should show an approximately correct melting point, and should give a fairly clear solution in warm dilute hydrochloric acid, without any oily residue.

A solution of  $\alpha$ -naphthylamine hydrochloride yields a violet precipitate with ferric chloride and other oxidising agents.

A brownish red precipitate of aminoazonaphthalene is produced by nitrous acid and its salts in a solution which is not too strongly acidified. In a strongly acidified solution, only colourless diazo-naphthalene salts are formed.

$\alpha$ -Naphthylamine is manufactured from naphthalene by the same series of reactions as is aniline from benzene.

II.  *$\beta$ -Naphthylamine* is distinguished from the preceding isomeride by its much higher melting point and by the lack of the unpleasant odour. The pure substance crystallises in colourless, odourless leaflets, melting point 112°, boiling point 294°, which sublime easily, are slightly soluble in water, and dissolve readily in alcohol or ether. It does not turn brown in the air. With acetic acid it forms an acetyl derivative, melting at 132°. Its salts crystallise well, and are sparingly soluble. Characteristic colorations are not produced in their solutions by oxidising agents. Nitrous acid produces, in solutions of the salts, a brick-red precipitate of  $\beta$ -aminoazonaphthalene, but in strongly acid solutions only the diazo compound is formed.

The commercial product usually consists of a hard, fused mass. It should not possess the odour of  $\alpha$ -naphthylamine, should show approximately the correct melting point, and should dissolve almost completely in dilute hydrochloric acid. Naphthol and dinaphthylamine may be present as impurities, and are detected by their insolubility in dilute hydrochloric acid.

$\beta$ -Naphthylamine is prepared by heating  $\beta$ -naphthol with ammonia, or sodium naphthoxide with ammonium chloride above 200°.

*Ethyl- $\alpha$ -naphthylamine*.—In the air the base is steel-blue by reflected, and brownish red by transmitted, light.<sup>1</sup>

Its specific gravity is 1.073 at 18°. <sup>2</sup>

<sup>1</sup> Bamberger and Helwig, *Ber.*, 1889, 22, 1311.

<sup>2</sup> Vaubel, *Chem. Zeit.*, 1903, 27, 278.

Behaviour on distillation :—

Distilling at 292°	10.0 c.c.	} at 745 mm.
„ 302°	9.5 „	
„ 304°	9.5 „	
„ 306°	3.0 „	
„ 308°	7.0 „	
„ 310°	21.0 „	
„ 314°	7.0 „	
„ 316°	9.0 „	
„ 318°	6.0 „	
„ 320°	5.0 „	}
„ 323°	10.0 „	
Residue	3.0 „	
<hr/> <hr/>		100.0 c.c.

*Ethyl-β-naphthylamine*, when freshly distilled, is a colourless, viscous liquid, the surface of which soon becomes brown on exposure to the air.<sup>1</sup>

It does not solidify in a freezing mixture; it boils without decomposition at 315°—316° under the atmospheric pressure, and at 305°/716 mm. and at 191°/25 mm.<sup>2</sup> Its specific gravity is 1.062 at 18°.<sup>3</sup>

Behaviour on distillation :<sup>4</sup>—

Distilling at 322°	12 c.c.	} at 745 mm.
„ 324°	4 „	
„ 328°	14 „	
„ 330°	8 „	
„ 334°	8 „	
„ 336°	50 „	}
Residue	4 „	
<hr/> <hr/>		100 c.c.

Vaubel<sup>5</sup> recommends a method of bromination for the estimation of the two ethylnaphthylamines. These substances or their sulphonic acids are being increasingly used in the preparation of dyes.

### 19. Phenyl-naphthylamines, C<sub>10</sub>H<sub>7</sub>.NH.C<sub>6</sub>H<sub>5</sub>.

The α-compound, which is obtained by heating aniline hydrochloride and α-naphthylamine or α-naphthol and aniline or aniline hydrochloride, is employed in the preparation of Victoria blue, etc.

The pure substance melts at 62°, and boils at 335°/258 mm. or 226°/15 mm. It is a very weak base.

The commercial product usually consists of a slightly brownish

<sup>1</sup> Bamberger and Müller, *Ber.*, 1889, **22**, 1297.

<sup>3</sup> Vaubel, *Chem. Zeit.*, 1903, **27**, 278.

<sup>2</sup> *Ibid.*

<sup>4</sup> *Ibid.*

<sup>5</sup> *Chem. Zeit.*, 1903, **27**, 278.

coloured cake. Its melting point and its appearance are criteria of its suitability.

*β-Phenylnaphthylamine*, melting point  $107^{\circ}5-108^{\circ}$ , boiling point  $395^{\circ}-395^{\circ}5$ , is obtained by heating *β*-naphthol and aniline hydrochloride or *β*-naphthol, aniline, and zinc-ammonia chloride.

## 20. Phenylenediamines, $C_6H_4(NH_2)_2$ .

I. *m-Phenylenediamine*, melting point  $63^{\circ}$ , boiling point  $287^{\circ}$ , is obtained by the reduction of dinitrobenzene, and is easily soluble in water. It is mostly used directly in solution, but the base is also brought on the market in the solid state, being used largely as a "developer" for those azo dyes which are diazotised and "developed" on the cotton fibre. It should not be too darkly coloured, and its aqueous solution should be clear. *m*-Phenylenediamine is employed in the manufacture of Bismarck brown, chrysoidine, and other dyes.

*m*-Tolylenediamine (prepared from dinitrotoluene), which is employed for the same purpose, is usually manufactured directly in aqueous solution, but is also to be obtained in the solid state. Its melting point is  $99^{\circ}$  and boiling point  $280^{\circ}$ .

II. *p-Phenylenediamine*, melting point  $147^{\circ}$ , boiling point  $267^{\circ}$ , is obtained by the reduction of *p*-nitroaniline and also of aminoazobenzene. It is used in the preparation of indulines, which are soluble in water, and is put on the market as the free base. It usually occurs in dark brown or black crystalline masses. Although the product is always superficially coloured, it should have an approximately correct melting point, should dissolve completely in hot dilute hydrochloric acid, and should be pale-coloured at a freshly fractured surface.

To distinguish between the hydrochlorides of *m*- and *p*-phenylenediamine, an aqueous solution of the former is treated with a drop of a 1 per cent. solution of acetaldehyde in 50 per cent. alcohol, acidified by acetic acid, warmed, and allowed to cool. A magnificent yellow colour, with a pronounced green fluorescence is produced. *p*-Phenylenediamine hydrochloride gives an orange-red coloration without fluorescence.<sup>1</sup>

## 21. Benzidine, $C_{12}H_8(NH_2)_2$ , *o*-Tolidine, $C_{14}H_{12}(NH_2)_2$ , and Dianisidine, $C_{12}H_6(OCH_3)_2(NH_2)_2$ .

These para-diamino-derivatives are used extensively in the preparation of azo colouring matters which dye cotton without a mordant.

Free benzidine crystallises in colourless leaflets, melting point  $127^{\circ}5-128^{\circ}$ ; tolidine melts at  $129^{\circ}$ .<sup>2</sup>

<sup>1</sup> L. Cuniassé, *Ann. Chim. Anal.*, 1899, 4, 156.

<sup>2</sup> Guitermann, *Ber.*, 1887, 20, 2017; Hirsch, *ibid.*, 1890, 23, 3225, gives  $126^{\circ}5$ .

Formerly both bases were brought on the market as the sparingly soluble sulphates, usually in the form of a paste. Now, however, the bases themselves, purified by distillation in a vacuum, are generally manufactured. Titration by a solution of sodium nitrite suffices for the estimation of the purity of these products (see Sodium Nitrite, p. 927).

The titration in the case of the sulphates must be performed in a moderately strongly acid solution, and after the addition of the solution of the nitrite the test should not be made with iodide-starch paper too soon, since the conversion of the solid sulphate into the diazo compound does not occur very rapidly.

In determining the quality of the bases, attention must be paid not only to the appearance, but also to the melting point, the complete solubility in dilute hydrochloric acid, and the possible presence of ash (zinc).

Benzidine<sup>1</sup> should not melt below 125°, and tolidine not below 120°.

These substances are often contaminated by other bases which are also attacked by the nitrite; in such cases the nitrite method does not give accurate results. In order to estimate these basic impurities, a solution of the benzidine or tolidine in hydrochloric acid is treated with sulphuric acid or a soluble sulphate, whereby the sulphates of the two bases are precipitated; the basic impurities in the filtrate are then estimated by the nitrite method. (This method gives only an approximate estimation, since the solubility of benzidine sulphate or tolidine sulphate in water is materially increased by the addition of hydrochloric acid.)

Another method for the estimation of benzidine and of tolidine depends on the behaviour of neutral aqueous solutions of the hydrochlorides of these bases towards a solution of iodine, mono-iodo-derivatives being produced.<sup>2</sup> An excess of iodine at the end of the reaction is detected by iodide-starch paper or by a solution of starch, the spotting test being used.

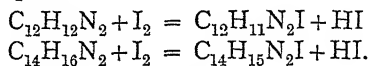
About 5 g. of the base are dissolved by warming with 5 c.c. of hydrochloric acid (sp. gr. 1.19) and water, and the solution, after cooling, is diluted to 500 c.c. Twenty-five c.c. of this solution are placed in a litre beaker and exactly neutralised by a solution of sodium hydrogen carbonate until a precipitate begins to be formed. The latter is redissolved by the addition of a single drop of very dilute hydrochloric acid. (The solution must be neutral, since iodobenzidine and iodo-tolidine are decomposed by acids with elimination of iodine.) The resulting solution is diluted to 500 c.c. with water, and is then titrated by *N*/20 solution of iodine, with continuous stirring. The iodo-derivative

<sup>1</sup> W. Vaubel, *Z. anal. Chem.*, 1896, 35, 163.

<sup>2</sup> Roesler and Glasmann, *Chem. Zeit.*, 1903, 27, 986.

is obtained as a dark blue precipitate. The completion of the reaction is determined by testing on a porcelain tile with a freshly prepared solution of starch, or with iodide-starch paper. The solution of iodine is standardised by the iodate method or by pure benzidine or tolidine thrice crystallised from benzene.

Two hundred and fifty-four parts of iodine represent 184 parts of benzidine and 212 parts of tolidine.



Vaubel<sup>1</sup> could not obtain trustworthy results by this method, and his experience has been confirmed in Gnehm's laboratory.

In the form of its diazo compound mixed with aluminium sulphate, *o*-dianisidine is put on the market under the name azophor blue D. Its examination is carried out by means of printing or dyeing trials. Benzidine, tolidine, and dianisidine are obtained by the reduction of nitrobenzene, *o*-nitrotoluene, and *o*-nitroanisole respectively with zinc dust and an alkali hydroxide, solution of the resulting hydrazo-compounds in hydrochloric acid (whereby the benzidine transformation is effected), and precipitation of the sulphates of the bases by sulphuric acid. For the preparation of the bases the sulphates are treated with sodium hydroxide and the base finally distilled under diminished pressure.

## 22. Nitroanilines, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ .

The meta- and the para- compounds are commercial substances, and are employed in the preparation of azo dyes.

1. *m*-Nitroaniline is obtained by the partial reduction of *m*-dinitrobenzene. It crystallises in flat, yellow needles, melting at  $114^\circ$ , and boiling at  $285^\circ$ , and is volatile with steam.

2. *p*-Nitroaniline, melting point  $147^\circ$ , forms yellow prisms with a superficial violet sheen. It is obtained by the nitration of acetanilide and the elimination of the acetyl group by acids or alkalis.

The meta- and para- compounds are formed in nearly equal quantities when aniline nitrate is introduced into cold concentrated sulphuric acid.

Both nitroanilines are moderately soluble in boiling water and dissolve slightly in cold water. They are easily soluble in acids.

The purity of the commercial products can be estimated by the nitrite method (see Sodium Nitrite); it is necessary, however, to add at least four equivalents of hydrochloric or sulphuric acid for each molecule of the base.

E. Blondel<sup>2</sup> recommends the dyeing method for testing the purity

<sup>1</sup> *Z. Farb. Ind.*, 1904, 3, 115.

<sup>2</sup> *Rev. Gen. Mat. Col.*, 1904, 8, 65; *Chem. Zeit. Rep.*, 1904, 85; see plate 7, in *Rev. Gen. Mat. Col.*, 1904, 1st April.

of *p*-nitroaniline; the presence of even 1.5 per cent. of *o*-nitroaniline can be detected easily by the difference of shade. The base under examination and the purest *p*-nitroaniline are diazotised separately. Cotton impregnated with  $\beta$ -naphthol is passed through the solutions, washed, and dried, and the colours are compared. Special care must be taken that the bases are diazotised completely.

To detect *m*-nitroaniline in the presence of *p*-nitroaniline, Liebmann<sup>1</sup> proceeds as follows: 0.25 g. of *p*-nitroaniline is placed in a flask provided with a Bunsen valve, and treated with hydrochloric acid and zinc dust until the solution has become colourless; this is then filtered and diluted to 250 c.c. When 10 c.c. of this solution are diluted to 50 c.c. and treated with one to two drops of a dilute solution of sodium nitrite, a faint yellow coloration only is produced. If the *p*-nitroaniline, however, contains *m*-nitroaniline, the solution is turned brown owing to the formation of Bismarck brown.

In the form of its diazo (or *isodiazo*) derivative *p*-nitroaniline constitutes the essential part of many commercial products which are used for the formation of azo dyes on the fabric (paranitraniline red or nitrosamine red) and for after treatment (for the so-called nitrol and nitrazol colours) in dyeing, and also to some extent in printing.

Azophor red PN, a yellowish powder, is *p*-nitrodiazobenzene hydrogen sulphate which has been converted into a solid product by the addition of dehydrated sodium or aluminium sulphate. Similar preparations are, nitrazol C, azogen red, and benzonitrol.

Paranitrodiazobenzene red is probably *p*-nitrodiazobenzene  $\alpha$ -naphthalenesulphonate, and the sodium salt of *p*-nitro*isodiazo*benzene is present in nitrosamine red, a 25 per cent. pale brown paste. Azophor orange is *m*-nitrodiazobenzene sulphate mixed with zinc sulphate. The quality of these products is determined by printing or dyeing trials.

### 23. Phenol (Carbolic Acid), $C_6H_5.OH$ .

Absolutely pure phenol occurs as a colourless, crystalline mass, melting at  $42^\circ$ . A very small amount of impurity—for example, a trace of water—appreciably lowers the melting point of the substance. Phenol boils at  $181^\circ.5$ , has a sp. gr. of 1.066, a peculiarly pungent odour, and is soluble in about fifteen parts of water. It readily absorbs water, and thereby loses the power of crystallising. Aqueous solutions of phenol are coloured violet by ferric chloride, and yield with bromine water a yellowish white precipitate of tribromophenol bromide. Nitric acid, according to its concentration, converts phenol into nitro-, dinitro-, or trinitro-phenol. When heated with oxalic and sulphuric acids it forms

<sup>1</sup> *J. Soc. Chem. Ind.*, 1897, 16, 294.

a red dye (rosolic acid). The methods for the identification and estimation of phenol are detailed on pp. 821 *et seq.*<sup>1</sup>

Phenol is used for the preparation of picric acid, rosolic acid, and of many azo dyes.

So-called "white crystallised carbolic acid" is usually employed technically. This melts at about 30°, and boils between 183° and 186° (see also this Vol., p. 812).

#### 24. Cresols, $C_7H_7.OH$ .

Three isomeric cresols are known:

1. *o-Cresol*, melting point 30°, boiling point 190°·8, is a colourless, crystalline mass. By prolonged fusion with potassium hydroxide it yields salicylic acid.

2. *m-Cresol* is a colourless liquid, boiling point 202°·8. It yields *m*-hydroxybenzoic acid by fusion with potassium hydroxide.

3. *p-Cresol*, melting point 36°, boiling point 201°·8, crystallises in colourless prisms. It is sparingly soluble in water, and develops a blue coloration with ferric chloride. Fusion with potassium hydroxide converts it into *p*-hydroxybenzoic acid.

The cresol isolated from coal tar contains about 40 per cent. of the meta-, 35 per cent. of the ortho-, and 25 per cent. of the para-isomeride.

For its examination, see this Vol., p. 813.

#### 25. Naphthols, $C_{10}H_7.OH$ .

$\alpha$ - and  $\beta$ -Naphthols are employed extensively for technical purposes. In consequence of the discovery of the azo dyes,  $\beta$ -naphthol, in particular, has become a substance of the utmost importance in the colour industry.

1.  *$\alpha$ -Naphthol*, melting point 94°, crystallises in colourless needles. It is somewhat soluble in cold water, more easily in hot, and dissolves readily in alcohol, ether, or benzene. Alkali hydroxides dissolve it easily, forming crystalline naphthoxides, from which, however, the naphthol is regenerated even by carbon dioxide or ammonium chloride.  $\alpha$ -Naphthol distils at 278°—280° with slight decomposition. The technical product is a fused, crystalline mass, the melting point of which is usually somewhat lower than that stated above; it is not free from  $\beta$ -naphthol.

The tests mentioned under  $\beta$ -naphthol are applicable, as a rule, for its examination (*cf.* p. 881). Its chief uses are for the preparation of dinitronaphthol and its sulphonic acids and for the manufacture of azo dyes.

2.  *$\beta$ -Naphthol* in the pure state forms colourless leaflets, melting

<sup>1</sup> *Cf.* also G. Candussio, "A new reagent for phenolic compounds." *Chem. Zeit.*, 1900, 24, 299.

at  $128^{\circ}$ . It boils with slight decomposition at  $285^{\circ}$  to  $290^{\circ}$ , and sublimes at much lower temperatures. It is slightly soluble in hot water, and dissolves easily in alcohol, benzene, or ether. Its behaviour towards alkalis is analogous to that of  $\alpha$ -naphthol. The technical product usually consists of almost colourless, fused, foliated, crystalline masses, and is, as a rule, very pure. •

In its examination, attention should be paid primarily to the melting point and the appearance. It should be almost colourless and should not turn brown in the air. Moreover, it should dissolve in dilute alkalis, giving a slightly coloured solution, and leaving only a very small residue.

Attention must also be given to the presence of any water, which is most easily determined quantitatively at the commencement of the distillation of a large quantity.

For the differentiation of  $\alpha$ - and  $\beta$ -naphthols, E. Leger<sup>1</sup> employs sodium hypobromite. A cold saturated aqueous solution is prepared by grinding the substance under examination with water in a mortar, and filtering the emulsion after some time. The solution of the hypobromite is made with 30 c.c. of sodium hydroxide (sp. gr. 1.33), 100 c.c. of water, and 5 c.c. of bromine. Ten c.c. of the aqueous solution of the naphthol are treated with a few drops of the hypobromite. In a solution of  $\alpha$ -naphthol a dirty violet precipitate is produced (the reaction is very sensitive); in a solution of  $\beta$ -naphthol a yellow colour is developed which gradually becomes greenish and then yellow again; in more dilute solutions of  $\beta$ -naphthol the yellow colour quickly disappears by shaking (the reaction is less sensitive than that of  $\alpha$ -naphthol).

When a saturated aqueous solution of both naphthols is diluted with an equal volume of water and shaken with two drops of the hypobromite solution, the  $\alpha$ -naphthol, but not the  $\beta$ -naphthol, gives this reaction.

In this way the presence of 1 per cent. of  $\alpha$ -naphthol in  $\beta$ -naphthol can be easily detected. Freshly prepared solutions must always be used.

According to Liebmann,<sup>2</sup> the presence of a small quantity of  $\alpha$ -naphthol in  $\beta$ -naphthol is detected in the following way:—

Fifteen c.c. of toluene are added to a solution of 0.144 g. in 5 c.c. of pure alcohol in a graduated cylinder; 0.14 g. of *p*-nitro-aniline is dissolved in 9 c.c. of dilute hydrochloric acid, and the solution is cooled in a freezing mixture, diazotised by 1 c.c. of *N*/1-nitrite solution, and poured into the solution of the naphthol. The mixture is shaken, and, after the addition of a little water, the two liquids are separated in a separating funnel, and the toluene solution

<sup>1</sup> *Bull. Soc. Chim.*, 1897 [iii.], 17, 546.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1897, 16, 294.



is agitated with 5 c.c. of sodium hydroxide; the colour is compared with the colours of solutions which have been prepared in the same way from  $\beta$ -naphthol containing a known amount of  $\alpha$ -naphthol. The colour of the solutions changes by keeping, and they must, therefore, be freshly prepared each time. The presence of 0.01 g. of  $\alpha$ -naphthol can be detected in this way.

G. Jorissen<sup>1</sup> distinguishes between  $\alpha$ - and  $\beta$ -naphthol by treating a trace of the substance in a test tube with 2 c.c. of a solution of iodine in potassium iodide (of the concentration of the usual alkaloid reagent) and adding an excess of aqueous sodium hydroxide.  $\beta$ -naphthol forms a colourless, clear solution whilst  $\alpha$ -naphthol yields a strongly violet, turbid liquid. When the  $\beta$ -naphthol contains  $\alpha$ -naphthol a more or less violet coloured liquid is obtained by the addition of the reagent mentioned.

Volcy-Boucher's<sup>2</sup> test is as follows:—0.5 g. of the substance is placed in a test tube and dissolved in the smallest possible quantity of alcohol (45 per cent.), added drop by drop. Two c.c. of 10 per cent. copper sulphate solution are added, and, after thorough shaking, 4 c.c. of a freshly prepared 10 per cent. solution of potassium cyanide. With  $\alpha$ -naphthol an abundant violet-red precipitate is obtained;  $\beta$ -naphthol yields a yellow precipitate. If now just sufficient alcohol is added to dissolve the precipitate, a rose-coloured liquid showing a violet reflexion will be obtained with the  $\alpha$ -compound, but a golden-yellow solution in the case of  $\beta$ -naphthol. Small proportions of  $\alpha$ -naphthol in  $\beta$ -naphthol may be detected by this process.

F. W. Küster's acidimetric estimation of  $\alpha$ - and  $\beta$ -naphthol depends on the formation of sparingly soluble picric acid compounds.<sup>3</sup>

When either of the naphthols is digested on the water-bath with a known volume of an aqueous solution of picric acid nearly saturated at the ordinary temperature, the naphthol slowly disappears and in its place a precipitate of the equivalent quantity of the picric acid compound is obtained, practically quantitatively in most cases. By titration with  $N/10$ -barium hydroxide and phenolphthalein (or lacmoid) as indicator, the amount of picric acid in the original aqueous solution and also that in an aliquot portion of the filtrate from the picrate can be determined, and from these values the amount of picric acid in the precipitate can be calculated. The last value multiplied by the necessary factor gives the amount of naphthol.

Since the digestion on the water-bath is necessarily performed in hermetically sealed vessels, the following method can be used.

The substance under examination and the measured volume of the

<sup>1</sup> *Ann. Chim. Anal.*, 1902, 7, 217.

<sup>2</sup> *Ibid.*, 1908, 13, 335.

<sup>3</sup> *Ber.*, 1894, 27, 1101. Cf. also Pelet-Jolivet and Henny, *Bull. Soc. Chim.*, 1909 [iv.], 5, 623.

standard solution of picric acid are placed in a flask of such a capacity that it is filled to the neck. A solution of picric acid, saturated at the ordinary temperature, is about  $N/20$ , and the measured volume must be such that a sufficient excess of picric acid remains in the solution at the end of the reaction, since only in this case is a quantitative precipitation of the molecular compound obtained. The flask must be strong enough to be evacuated without risk. It is closed by a good rubber stopper through which passes a tube about 7 cm. long, which can be moved without much trouble and is sealed at its lower end. About 1.5 cm. above this end a small hole is blown, through which the flask can be evacuated when the tube is pushed in far enough. When the evacuation is complete, the tube is drawn so far upwards, whilst the pump is still working, that its closed end is level with the lower surface of the stopper, whereby communication between the interior of the flask and the atmosphere is cut off. If everything fits properly and the stopper and the tube have been slightly moistened before being inserted, the vacuum in the flask can be maintained for a whole day.

When the reaction is complete, the flask is allowed to cool, and to stand overnight. Before the stopper is removed air is allowed to enter the flask by lowering the tube.

(Since the compound of  $\beta$ -naphthol and picric acid is soluble in water, it must be remembered, in calculating the results, that on the average about 0.0075 g. of  $\beta$ -naphthol remains in solution for every 100 c.c. of picric acid solution employed.) This method is also applicable for the estimation of naphthalene and other hydrocarbons.

The iodometric method of J. Messinger and G. Vortmann<sup>1</sup> can also be used for the titration of  $\beta$ -naphthol. Since the equivalence of iodine and  $\beta$ -naphthol varies with the concentration of the naphthol solution, F. W. Küster's<sup>2</sup> correction tables must be employed, by the aid of which correct values can be obtained.

Large quantities of  $\beta$ -naphthol are used in the preparation of red and of orange-yellow azo dyes.

The naphthols are obtained by fusing the respective naphthalene-sulphonic acids with sodium hydroxide. Both naphthols yield a series of sulphonic acids, some of which are prepared for the purpose of manufacturing dyes. Several of them are put on the market.

## 26. Resorcinol, $C_6H_4(OH)_2$ .

Pure resorcinol forms colourless, transparent, rhombic crystals, melting at  $110^\circ$ . It distils and partly decomposes at  $271^\circ$ , and is easily soluble in water, alcohol, and ether, and somewhat sparingly in so hot benzene. Its aqueous solution has a sweet taste and is coloured a deep violet by ferric chloride. The product obtained by heating resorcinol

<sup>1</sup> *Ber.*, 1890, 23, 2754.

*Ibid.*, 1894, 27, 1905.

and phthalic anhydride at about  $200^{\circ}$  dissolves in dilute alkalis or in ammonium hydroxide with a magnificent green fluorescence (due to fluorescein).

Commercial resorcinol is a fairly pure substance. It consists of a slightly coloured, dry, crystalline mass which does not turn brown in the air: this is the best guarantee of its purity. In addition, it should have the correct melting point, give a clear and only slightly coloured solution in water, and should not have the odour of phenol, or at all events only to a small extent. The amount of water is determined by drying a powdered sample over sulphuric acid. Its chief uses in the colour industry are for the preparation of eosin dyes, of *m*-aminophenol derivatives, and occasionally of azo dyes.

Resorcinol is prepared by fusing the various benzenedisulphonic acids with sodium hydroxide. It is extracted from the acidified melt by ether or amyl alcohol, and is purified by distillation in a vacuum.

### 27. Sulphanilic Acid (*p*-Aminobenzenesulphonic Acid), $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$ .

Sulphanilic acid is an intermediate product in the preparation of various azo dyes, particularly of orange II. and orange IV.; it is also used in the production of *p*-phenylhydrazinesulphonic acid.

In the pure state it forms colourless, hydrated crystals, which effloresce above  $100^{\circ}$  and become anhydrous. It is slightly soluble in cold water, and comparatively easily in hot. It reacts with alkalis to form easily soluble salts, which crystallise well and are decomposed by hydrochloric or sulphuric acid. It yields *p*-benzoquinone by oxidation by potassium bichromate and sulphuric acid.

Sulphanilic acid, being a moderately strong acid, can be estimated volumetrically. In order to remove the free sulphuric acid, which is a frequently occurring impurity, the weighed quantity of the substance is moistened with a solution of barium chloride and heated on the water-bath to remove the liberated hydrochloric acid. The residue is then dissolved in a known volume of *N*/1 alkali, the excess of which is titrated by *N*/10 acid; 1 c.c. of the *N*/1 alkali represents 0.173 g. of sulphanilic acid.

A more trustworthy method is the titration of the sulphanilic acid by sodium nitrite (*cf.* Sodium nitrite, p. 927).

Account must be taken in this case of the presence of any aniline which, after the addition of an excess of alkali, is removed by distillation with steam before titrating.

K. Brenzinger's method<sup>1</sup> for the estimation of sulphanilic acid depends on the fact that the sulphonic acid group is eliminated very easily and quantitatively by bromine. The method is applicable for

<sup>1</sup> *Z. angew. Chem.*, 1896, 9, 131.

the estimation of sulphanilic acid, alone or mixed with metanilic acid.

*Estimation of pure Sulphanilic Acid.*—Dissolve 17.3 g. (1/10 mol.) of anhydrous sulphanilic acid in a litre of water. If the solution is alkaline, it is faintly acidified by hydrochloric acid. Saturated bromine water is added to 100 c.c. of this solution until iodide-starch paper indicates an excess of bromine, which should remain for at least fifteen to twenty minutes. After twenty minutes, the solution is rendered slightly alkaline by pure sodium carbonate solution, whereby the excess of bromine is destroyed, and, particularly with impure products, a liquid which can be filtered more easily is obtained. It is advisable, but not absolutely necessary, to warm the alkaline solution for a short time. The sulphuric acid in the filtrate is estimated in the usual way. The operations of precipitation, filtration, and washing, however, must be performed with hot liquids, especially when metanilic acid is present. Keeping the liquid hot for two to three hours is quite sufficient.

*Estimation of Sulphanilic Acid in the presence of Metanilic Acid* is performed just as in the case of sulphanilic acid alone.

If the substance contains only sulphanilic and metanilic acids, their total amount can be estimated by diazotisation, provided that no other compounds are present which are attacked by the nitrite. By subtracting from the total the amount of sulphanilic acid determined by the bromine method, an accurate estimation of the metanilic acid is obtained.

Sulphanilic acid is put on the market in the form of its beautifully crystalline sodium salt, which has the formula,  $C_6H_6O_3NSNa, 2H_2O$  (mol. wt. 231).

Sulphanilic acid is obtained by heating aniline with the calculated quantity of sulphuric acid at  $180^\circ$ .

The isomeric *m*-aminobenzenesulphonic acid is prepared by the reduction of nitrobenzenesulphonic acid, and is also used technically. It differs from the para-isomeride described above in its greater solubility. Bromine converts it into tribromoanilinesulphonic acid.

Its amount in the crude product is also best estimated by titration with sodium nitrite.

## 28. Naphthionic Acid, $NH_2 \cdot C_{10}H_6 \cdot SO_3H$ .

1-Naphthylamine-4-sulphonic acid is also largely used in the preparation of azo dyes. The beautifully crystalline sodium salt is usually prepared. Since the acid is almost insoluble in water, its amount in the crude sodium salt can be fairly accurately determined by precipitation with hydrochloric acid, and weighing the well-washed precipitate.

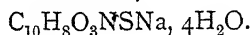
Here also, however, a more trustworthy method is the titration by

sodium nitrite, which can also be performed on the precipitated naphthionic acid, and is preferable to the gravimetric method.

The presence of unaltered naphthylamine is detected by the turbidity as well as by the odour of the alkaline solution, and with greater certainty by extracting the latter with ether.

Naphthionic acid is prepared by heating  $\alpha$ -naphthylamine with sulphuric acid.

Sodium naphthionate contains four molecules of water of crystallisation, corresponding with the formula,



For the estimation of the naphthol- and of the naphthylamine-sulphonic acids, Vaubel proposes the following method<sup>1</sup>:—It depends on the fact that the hydroxy- and amino- derivatives of benzene and naphthalene are able, under suitable conditions, to absorb one or more atoms of bromine in the ortho- and the para- positions to the hydroxyl or the amino- group, provided that no other influence is being exerted. The same behaviour is exhibited by the naphthol- and the naphthylamine-sulphonic acids when the sulphonic acid group does not occupy a position in which it hinders the entrance of the bromine.

In performing the estimation, an aqueous solution of a weighed quantity of the impure sulphonic acid is treated with potassium bromide and a sufficient amount of sulphuric acid, and standard potassium bromate is run in until a persistent excess of bromine is observed. The operation is performed at the ordinary temperature. With regard to their capacity of absorbing bromine, the sulphonic acids can be arranged in three classes:—

1. Those which absorb at the most only one atom of bromine and give a sharp end-point.

2. Those which absorb more than one atom of bromine, and give an indistinct end-point in consequence of the slower absorption of the second and the third bromine atoms.

3. Those which absorb little or no bromine under the conditions mentioned above.

The first class includes—

A. The following  $\alpha$ - and  $\beta$ -naphthylaminesulphonic acids:—

	NH <sub>2</sub> .	SO <sub>3</sub> H.	SO <sub>3</sub> H.
a. Orthonaphthionic acid . . . . .	I	2	...
b. Naphthionic acid . . . . .	I	4	...
c. Dahl's disulphonic acid II. . . . .	I	4	6
d. " " " III. . . . .	I	4	7
e. $\alpha$ -Naphthylamine- $\delta$ -disulphonic acid . . . . .	I	4	8
f. Amino-R-acid . . . . .	2	3	6
g. $\beta$ -Monosulphonic acid (2 Br) . . . . .	2	5	...
	NH <sub>2</sub> .	NH <sub>2</sub> .	SO <sub>3</sub> H.
h. Naphthylenediaminesulphonic acid . . . . .	I	6	4

<sup>1</sup> *Chem. Zeit.*, 1893, 17, 1265, 1897.

B. The following  $\alpha$ - and  $\beta$ -naphtholsulphonic acids:—

	OH.	SO <sub>3</sub> H.	SO <sub>3</sub> H.	SO <sub>3</sub> H.
<i>a.</i> Nevile and Winther's acid . . . . .	1	4	...	...
<i>b.</i> $\alpha$ -Naphtholdisulphonic acid . . . . .	1	4	8	...
<i>c.</i> Schäffer's acid . . . . .	2	6	...	...
<i>d.</i> F-acid . . . . .	2	7	...	...
<i>e.</i> R-acid . . . . .	2	3	6	...
<i>f.</i> $\beta$ -Naphtholtrisulphonic acid . . . . .	2	3	6	8

(In several of these acids, for example, the 1:4:8 and the 2:3:6:8, bromine is absorbed rather slowly.)

To the second class belong—

A. The following  $\alpha$ - and  $\beta$ -naphthylaminesulphonic acids:—

	NH <sub>2</sub> .	SO <sub>3</sub> H.	SO <sub>3</sub> H.
<i>a.</i> $\alpha$ -Naphthylaminesulphonic acid (3 Br) . . . . .	1	7	...
<i>b.</i> $\alpha$ -Naphthylaminesulphonic acid S (2 Br) . . . . .	1	8	...
<i>c.</i> $\alpha$ -Naphthylamine- $\beta$ -disulphonic acid (2 Br) . . . . .	1	3	7
<i>d.</i> $\alpha$ -Naphthylaminedisulphonic acid Kalle (2 Br) . . . . .	1	2	7
<i>e.</i> Brönner's acid (3 Br) . . . . .	2	6	...
<i>f.</i> $\beta$ -Naphthylamine- $\delta$ -sulphonic acid I (3 Br) . . . . .	2	7	...

B. The following naphtholsulphonic acid —

	OH.	O <sub>3</sub> H.	SO <sub>2</sub> H.
$\alpha$ -Naphtholsulphonic acid S . . . . .	1	8	...

To the third class belong—

A. The following  $\beta$ -naphthylaminesulphonic acids:—

	NH <sub>2</sub> .	SO <sub>3</sub> H.	SO <sub>3</sub> H.
<i>a.</i> $\beta$ -Naphthylamine- $\alpha$ -sulphonic acid . . . . .	2	8	...
<i>b.</i> Amino-G-acid . . . . .	2	6	8

B. The corresponding naphtholsulphonic acids:—

	OH.	SO <sub>3</sub> H.	SO <sub>3</sub> H.
<i>a.</i> Crocein acid . . . . .	2	8	...
<i>b.</i> G-acid . . . . .	2	6	8

The last acids, the 2:8- and the 2:6:8- derivatives, absorb bromine at a higher temperature, and the property can be employed for their estimation. At 65°–75° they readily absorb one atom of bromine, and any volatilisation of the halogen is so inconsiderable as not to affect the estimation. The temperature must not be allowed to fall much below 65°, since it is then difficult to detect the end-point.

Mixtures of these acids and the corresponding 2:6- or 2:3:6- derivatives cannot, however, be estimated by first determining the Schäffer's acid and the R-acid at the ordinary temperature, and then warming and estimating the 2:8- and the 2:6:8- acids, because the presence of the G-acid or the crocein acid renders it difficult to detect the end-point at the conclusion of the first reaction.

Such mixtures can be estimated, however, by determining the total sulphonic acid by bromination, and then estimating the R-acid or the Schäffer's acid by coupling with diazo compounds.

A method which has been much used for the estimation of naphthol- and naphthylamine-sulphonic acids consists in titrating (in the case of the former acids) an alkaline solution with a standard solution of diazo-benzene or xylene. During this titration, sodium chloride is added to the solution in order to precipitate the dyestuff which is formed, and the course of the titration is followed by placing a drop of the mixture on filter paper and observing the reaction of the colourless rim when a drop of diazo solution or of a solution of a naphtholsulphonic acid (usually R-salt) is brought into contact with it. The diazo solution is added to the alkaline solution of naphtholsulphonic acid until no reaction further is obtained with it in the "spotting" test. This method is stated to give inaccurate results, but Bucherer and also Schwalbe have shown that when diazotised *p*-nitraniline is used in acid solution exact figures are obtained.

Bucherer's<sup>1</sup> method is as follows:—Nitrosamine paste, which usually contains 25 per cent. of the compound  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{ONa} + \text{H}_2\text{O}$ , is first washed free from nitrous acid by means of a saturated salt solution; 82.8 g. of it are stirred with 200 c.c. of water, and treated with 30 to 40 c.c. of concentrated hydrochloric acid. The resulting solution is filtered and made up to 1 litre. If the diazo solution is prepared direct from *p*-nitroaniline, 13.8 g. of the latter are gently warmed with 16 g. of concentrated hydrochloric acid and 20 c.c. of water. The warm solution is then poured into a mixture of 500 g. of ice, 8 g. of concentrated hydrochloric acid, and 50 c.c. of nitrite solution containing 6.9 g. of sodium nitrite. After stirring for a short time, an almost clear solution is obtained, which is filtered after a further fifteen minutes. The filtrate is diluted to 1 litre, protected from light, and standardised by titration with a very dilute solution of  $\beta$ -naphthol in presence of sodium acetate or bicarbonate. Most of the naphthol and naphthylamine mono- and di-sulphonic acids may be accurately analysed by titration with diazotised *p*-nitroaniline in presence of sodium acetate or bicarbonate, but those naphthylaminesulphonic acids which combine with difficulty or not at all with diazo compounds, must be titrated with sodium nitrite according to the usual method. In carrying out the analysis, such an amount of the component is taken as will require about 20 to 25 c.c. of the diazo solution; the usual precaution of adding salt to precipitate the azo dyestuff must also be observed.<sup>2</sup>

## 29. Benzyl Chloride, $\text{C}_6\text{H}_5 \cdot \text{CH}_2\text{Cl}$ .

Pure benzyl chloride is a colourless liquid boiling at  $176^\circ$ , which affects the eyes and has a penetrating odour. Since the chlorine atom is attached to the carbon of the methyl group, benzyl chloride

<sup>1</sup> *Z. angew. Chem.*, 1907, 20, 877.

<sup>2</sup> Cf. also Schwalbe, *Z. angew. Chem.*, 1907, 20, 1098.

resembles the alkyl chlorides of the aliphatic series and its chlorine is easily replaceable by other groups. On this property depends its application in the preparation of benzyl derivatives, especially of benzylated methyl violets.

The quality of technical benzyl chloride has improved considerably in the course of time. It must be colourless, have a sp. gr. of 1.106 to 1.110, and distil, to the extent of about 96 per cent., between 174° and 179°, without the evolution of hydrogen chloride.

Benzyl chloride is prepared by the action of chlorine on boiling toluene; chlorine gas is passed in until the weight of the product has been increased by the theoretical amount.

### 30. Benzylidene Chloride, $C_6H_5 \cdot CHCl_2$ .

Pure benzylidene chloride is a colourless liquid, boiling at 206°, with a penetrating odour. Technical benzylidene chloride (benzal chloride), which is employed in the preparation of benzaldehyde, benzoic acid, and cinnamic acid, leaves much to be desired, even now, in the matter of purity. The quality may be regarded as satisfactory when the substance has approximately the correct boiling point and the theoretical percentage of chlorine.

It is obtained from toluene in the same way as benzyl chloride, but the chlorination is more prolonged.

### 31. Benzotrichloride, $C_6H_5 \cdot CCl_3$ .

The pure substance is a colourless liquid, boiling at 213°—214°. Benzotrichloride has played a transitory part in the colour industry, being the original substance by means of which malachite green was produced.

What has been said of benzyl and benzylidene chlorides, is true also of the technical product. Of chief importance is the fact that it cannot be obtained free from substances containing chlorine in the benzene nucleus.

The preparation of benzotrichloride is analogous to that of benzyl and benzylidene chlorides. In this case the chlorination is prolonged even more than in that of benzylidene chloride, and the product is finally rectified in a vacuum.

### 32. Benzaldehyde, $C_6H_5 \cdot CHO$ .

Pure benzaldehyde is a highly refractive liquid, boiling point 180°, sp. gr. 1.0504, which is miscible in all proportions with alcohol and ether, but not with water. It shows the general behaviour of aldehydes; it is oxidised to benzoic acid moderately rapidly in the air, and forms with sodium hydrogen sulphite a crystalline additive compound which is easily soluble in water. It is reduced to benzyl



alcohol by nascent hydrogen. When heated with alcoholic potassium hydroxide, it yields benzyl alcohol and benzoic acid.

Benzaldehyde is manufactured in large quantities for the preparation of green dyes, and is put on the market in a state of considerable purity. For its examination, the boiling point and the specific gravity should be determined, but these alone are not sufficient, as they are affected by the benzoic acid which is always present. The distillation should be always performed in a current of carbon dioxide or hydrogen to prevent the formation of this acid. Benzaldehyde should be colourless, have a sp. gr. 1.052 to 1.055, and distil completely between 176° to 180° in a current of hydrogen.

It must give a clear mixture with concentrated sulphuric acid without a strong brown coloration, and dissolve in a solution of ammonium hydrogen sulphite without any oily residue.

To estimate any benzoic acid which may be present, 50 c.c. of the benzaldehyde are shaken with 10 c.c. of *N*/1 sodium hydroxide and water, and phenolphthalein as indicator, and the excess of the alkali is titrated by *N*/1 acid; 1 c.c. of *N*/1 sodium hydroxide represents 0.122 g. of benzoic acid. Benzaldehyde is prepared by treating benzylidene chloride with calcium carbonate or sodium hydroxide and water.

### 33. Benzoic Acid, $C_6H_5.CO_2H$ .

Pure benzoic acid crystallises in small colourless needles or leaflets with a faint peculiar odour. It melts at 120° and boils at 250°, but sublimes even below the temperature of the water-bath. It is sparingly soluble in cold, more readily in hot water, and dissolves very easily in alcohol or ether. Its salts are mostly very readily soluble in water. With a neutral solution of ferric chloride, they yield ferric benzoate in the form of a reddish precipitate.

Benzoic acid is employed in the colour industry for the preparation of aniline blue and of nitro- or amino-benzoic acids.

Commercial benzoic acid should be colourless, should volatilise without residue, have the correct melting point, and give clear solutions in dilute ammonium hydroxide, benzene, and ether.

A product containing chlorine must be rejected.

Since benzoic acid distinctly affects litmus, it can be titrated by *N*/1 alkali hydroxides. On account of its sparing solubility in water, it is advisable to dissolve the acid in an excess of the alkali, and to titrate back with *N*/10 acid.

When benzoic acid is to be employed in the preparation of aniline blue, a trial of its suitability for this purpose is necessary, because commercial benzoic acid often contains impurities which escape detection by analysis and yet are frequently very troublesome in the preparation of the blue.

### 34. Salicylic Acid, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ .

Salicylic acid is used extensively in the preparation of azo dyes.

The pure acid is colourless and odourless, and crystallises in needles melting at  $156^\circ$ .

It is only slightly soluble in cold water (about 1:500 at  $15^\circ$ ), but dissolves more readily in boiling water (about 1:13). Its aqueous solution is coloured violet by ferric chloride.

Salicylic acid for medicinal purposes is almost chemically pure, and the same may be said for the product which is employed in the colour industry.

Since salicylic acid behaves like a monobasic acid (its dibasic salts have an alkaline reaction), it can be estimated alkalimetrically. Attention should also be given to the possible presence of ash.

Salicylic acid is prepared by the Kolbe-Schmitt method by the action of carbon dioxide on sodium phenoxide.

### 35. Gallic Acid, $\text{C}_6\text{H}_2(\text{OH})_3 \cdot \text{CO}_2\text{H}$ .

Gallic acid is trihydroxybenzoic acid, and therefore is best considered here, although it is not a product of coal tar. It finds many applications in the colour industry, as, for example, in the preparation of gallocyanine (and analogous dyes), galloflavin, and anthragallol.

In the pure state it forms colourless needles which contain one molecule of water.

The anhydrous acid melts at about  $220^\circ$ . Its solution gives a bluish black precipitate with ferric chloride. It cannot be estimated alkalimetrically, since its alkaline solution rapidly turns brown in the air. Its quality, therefore, is judged by the appearance, the possible presence of ash, etc.

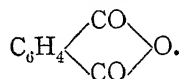
Gallic acid is obtained from tannin and various other tannic acids by boiling with dilute acids or by a specific fermentation.

**Tannin** (Tannic acid), an anhydride of gallic acid, is extensively used in dyeing and printing, especially as a mordant for basic dyes. Of the many methods proposed for its examination, one only is conclusive, namely, comparative dye-trials and print-trials with the substance in question and products of known quality.

Tannin is a faintly yellow, amorphous powder. It should dissolve moderately easily in water, giving a slightly coloured solution. It is also brought on the market as so-called "crystallised tannin," and "needle tannin."

The detection of tannin on the fabric is described by A. Menger.<sup>1</sup>

<sup>1</sup> *Färber-Zeit.*, 1903, 14, 435.

36. Phthalic Acid,  $C_6H_4(CO_2H)_2$ , and Phthalic Anhydride,

Pure phthalic acid crystallises in colourless leaflets or stout prisms, melting at  $213^\circ$ . It is sparingly soluble in cold water, and dissolves easily in hot water, alcohol, or ether. When heated at about  $130^\circ$ , it decomposes gradually into phthalic anhydride and water. It is commonly and erroneously stated in the literature that the formation of the anhydride only begins above  $200^\circ$ . (The fact is given correctly in Kolbe's *Organic Chemistry*.) The anhydride forms long colourless needles having a faint characteristic odour, melting at  $128^\circ$ , and boiling at  $277^\circ$ , but sublimes below its melting point. It dissolves in hot water, regenerating the acid.

Technically, the name "phthalic acid" always denotes phthalic anhydride, which is brought on the market in the sublimed state and plays an important part in the preparation of indigo and the phthaleins (eosin, rhodamine, gallein, etc.). Commercial phthalic anhydride may be considered as sufficiently pure when it consists of colourless needles which have the correct melting point, are soluble in benzene, and volatilise without residue.

Phthalic acid is prepared by the oxidation of naphthalene by sulphuric acid in the presence of mercuric sulphate. Phthalic anhydride is obtained from the crude acid by sublimation.

Dichlorophthalic acid is obtained from the chlorinated chloronaphthalenes, and tetrachlorophthalic acid by heating phthalic anhydride with antimony pentachloride in a current of chlorine. These acids are also utilised in the production of eosin dyes. Dichlorophthalic acid melts at  $183^\circ$ — $185^\circ$ , and tetrachlorophthalic acid melts and yields the anhydride at  $250^\circ$ .

37. Anthraquinone,  $C_{14}H_8O_2$ .

Pure anthraquinone forms lustrous, bright yellow needles, melting at  $277^\circ$ . It sublimes at a slightly higher temperature, and boils above  $382^\circ$ . It is insoluble in water, slightly soluble in ether, alcohol, or cold benzene, more easily in hot benzene, and dissolves readily in hot glacial acetic acid. It dissolves unchanged in hot nitric acid (sp. gr. 1.4) and also in concentrated sulphuric acid. It is converted into anthracene by heating with zinc dust or concentrated hydriodic acid. When anthraquinone is heated with alcoholic alkali hydroxide and zinc dust or sodium amalgam, the solution acquires a reddish violet colour, but quickly becomes colourless again in the air. The colour is green when absolutely anhydrous

alcohol is used, but is changed to violet by the slightest trace of water.

Anthraquinone is the first intermediate product in the conversion of anthracene into alizarin. It rarely comes on the market, but is prepared in the alizarin works. Sublimed anthraquinone is always employed, the purity varying usually between 98 to 99 per cent. Luck's method (p. 805) can be used for estimating the purity of anthraquinone. In this method the impurities, by further oxidation, are destroyed or converted into substances which are soluble in alkalis.

H. Bassett<sup>1</sup> suggests boiling the anthraquinone for some time with a solution of chromic acid and nitric acid; pure anthraquinone should not lose in weight, whilst the product prepared from commercial anthracene may lose 2 per cent. or more. Other tests are the melting point, the appearance, and also complete volatilisability.

Anthraquinone is prepared by treating anthracene with a mixture of potassium or sodium bichromate and dilute sulphuric acid. The crude product is purified by solution in warm sulphuric acid, precipitation by water, and finally by sublimation with steam.

## B. OTHER RAW MATERIALS

### 1. Methyl Alcohol (Wood Spirit), $\text{CH}_3\cdot\text{OH}$ .

Pure methyl alcohol is a mobile, colourless liquid, with a characteristic alcoholic odour and a burning taste; it is miscible in all proportions with water, ether, and alcohol. It boils at  $66^\circ\text{--}67^\circ$  and has a sp. gr. of 0.798 at  $0^\circ$ . It combines with calcium chloride and also with anhydrous barium oxide to form crystalline compounds which are decomposed by water and in which it appears to act like water of crystallisation.

Methyl alcohol is employed in the colour industry in the preparation of dimethylaniline, formaldehyde, and also of methyl chloride, bromide, iodide, and sulphate, which are used for various purposes. Its examination is of the utmost importance, since the alcohol must be very pure, especially for the preparation of dimethylaniline. The boiling point and the specific gravity afford some evidence as to its quality, but are by no means sufficient, since, in particular, acetone, a common impurity of wood spirit, closely resembles the alcohol in these properties.

The following table of the specific gravity of mixtures of pure methyl alcohol and water is given by A. Doroszewski and

<sup>1</sup> *Chem. News*, 1896, 73, 178.

M. Roshdestwenski;<sup>1</sup> the percentages of methyl alcohol are by weight.

Methyl alcohol.	Spec. Grav. at 15°/15°.	Methyl alcohol.	Spec. Grav. at 15°/15°.	Methyl alcohol.	Spec. Grav. at 15°/15°.
per cent.		per cent.		per cent.	
0	1.00000	34	0.94817	68	0.88048
1	0.99814	35	0.94653	69	0.87816
2	0.99630	36	0.94487	70	0.87584
3	0.99457	37	0.94319	71	0.87347
4	0.99285	38	0.94149	72	0.87109
5	0.99116	39	0.93976	73	0.86868
6	0.98950	40	0.93802	74	0.86622
7	0.98787	41	0.93625	75	0.86376
8	0.98633	42	0.93447	76	0.86126
9	0.98480	43	0.93266	77	0.85876
10	0.98327	44	0.93082	78	0.85626
11	0.98179	45	0.92896	79	0.85374
12	0.98031	46	0.92708	80	0.85122
13	0.97887	47	0.92517	81	0.84868
14	0.97745	48	0.92323	82	0.84610
15	0.97603	49	0.92128	83	0.84348
16	0.97462	50	0.91932	84	0.84082
17	0.97322	51	0.91733	85	0.83815
18	0.97181	52	0.91531	86	0.83548
19	0.97040	53	0.91328	87	0.83280
20	0.96899	54	0.91124	88	0.83010
21	0.96758	55	0.90918	89	0.82740
22	0.96617	56	0.90710	90	0.82468
23	0.96476	57	0.90500	91	0.82196
24	0.96335	58	0.90289	92	0.81921
25	0.96192	59	0.90075	93	0.81639
26	0.96047	60	0.89859	94	0.81356
27	0.95901	61	0.89641	95	0.81070
28	0.95752	62	0.89419	96	0.80784
29	0.95601	63	0.89195	97	0.80498
30	0.95449	64	0.88968	98	0.80213
31	0.95296	65	0.88739	99	0.79929
32	0.95139	66	0.88510	100	0.79647
33	0.94979	67	0.88280		

A very convenient method for the estimation of methyl alcohol has been given by Krell<sup>2</sup> and elaborated by Grodzky and Kraemer.<sup>3</sup> It depends on the fact that methyl alcohol is converted quantitatively into methyl iodide by phosphorus di-iodide, whilst the impurities react in a different manner.<sup>4</sup>

## 2. Methyl Chloride, CH<sub>3</sub>Cl.

At ordinary temperatures and pressures, methyl chloride is a colourless gas which has a pleasant ethereal odour and burns with a green-edged flame. It condenses to a colourless, mobile liquid at 22° under atmospheric pressure, or at the ordinary temperature under a pressure of about five atmospheres. Methyl chloride is dissolved slightly

<sup>1</sup> *J. Russ. Phys. Chem. Soc.*, 1909, 41, 154; *J. Soc. Chem. Ind.*, 1910, 29, 173.

<sup>2</sup> *Ber.*, 1873, 6, 1310.

<sup>3</sup> *Ibid.*, 1874, 7, 1492.

<sup>4</sup> F. Zetche, *Pharm. Centr.*, 1903, 44, 505; W. Vaubel and O. Scheuer, *Z. angew. Chem.*, 1905, 18, 214; G. Keppeler, *ibid.*, 464.

by water, but very easily by methyl or ethyl alcohol. It is brought on the market in the liquefied state in large copper or iron cylinders, and is used for the methylation of aniline, for the conversion of methyl violet into methyl green, and for other purposes. The commercial product is usually almost completely pure. It should volatilise rapidly and completely in an open vessel without leaving a malodorous residue.

### 3. Methyl Bromide, $\text{CH}_3\text{Br}$ .

Methyl bromide is used in certain cases instead of the chloride for the purpose of methylation, and then is usually prepared by warming sodium bromide with wood spirit and sulphuric acid.

It is a colourless, mobile liquid with a burning taste and a pleasant, ethereal odour, somewhat resembling that of chloroform. It boils at  $4^\circ.5$  and has a sp. gr. of 1.732 at  $0^\circ$ . It should volatilise rapidly in an open vessel without leaving a residue. The greatest care must be exercised in its use, on account of its poisonous nature.

### 4. Methyl Iodide, $\text{CH}_3\text{I}$ .

Methyl iodide is a colourless liquid, boiling point  $44^\circ$ , sp. gr. 2.199 at  $0^\circ$ , which is slowly coloured brown by light. It has a pleasant, ethereal odour, recalling that of chloroform. Methyl iodide was formerly a most important substance in the colour industry, and was used particularly for the preparation of iodine green and iodine violet, but now has a very limited application.

In testing it a determination of the boiling point should be made. When methyl iodide is exceptionally colourless and does not become coloured even by long exposure to light, it usually contains phosphorus. The presence of the latter is more certainly detected when the addition of a particle of iodine does not produce a yellowish brown colour. Traces of sulphur compounds are often present, and are betrayed by an unpleasant odour of leeks. On account of its poisonous nature, methyl iodide, particularly in the gaseous state, must be used with caution.

### 5. Methyl Sulphate, $(\text{CH}_3)_2\text{SO}_4$ .

This is prepared by the action of fuming sulphuric acid or chlorosulphonic acid on methyl alcohol.

It is a colourless liquid which has a very irritating action on the skin and is poisonous. It boils at  $188^\circ$  and has a sp. gr. of 1.324 at  $22^\circ$ .

### 6. Ethyl Bromide, $\text{C}_2\text{H}_5\text{Br}$ .

Ethyl bromide is a colourless, mobile liquid, boiling point  $38^\circ.8$ , sp. gr. 1.47, with a pleasant ethereal odour. The boiling point and the specific gravity are of chief importance in its examination.

Bromal and bromoform are occasionally present as impurities, but

are easily detected, however, by their higher boiling point. Compounds of sulphur can be recognised by their odour. Any ether present can be removed by shaking with concentrated sulphuric acid.

Ethyl bromide is prepared most readily by distilling sodium bromide or ferrous bromide with alcohol and sulphuric acid.

### 7. Ethyl Iodide, $C_2H_5I$ .

Ethyl iodide is a colourless liquid, boiling point  $72^\circ$ , sp gr. 1.975 at  $0^\circ$ , which becomes brown in the light and has an odour resembling that of chloroform. Ethyl iodide finds little application, since Hofmann's violet, which was formerly made by its aid, has been supplanted by methyl violet, and other reagents, preferably the cheaper ethyl bromide or chloride or diethyl sulphate, are used for ethylation. The statements given concerning the examination of methyl iodide are applicable to ethyl iodide.

### 8. Acetic Acid, $CH_3 \cdot CO_2H$ .

Pure acetic acid is a colourless, strongly acid liquid boiling at  $118^\circ$  and having a sp. gr. of 1.0553 at  $15^\circ$ . At low temperatures it solidifies to a mass of crystalline leaflets, melting at  $17^\circ$ .

The specific gravity increases at first by the addition of water, reaching a maximum, 1.075 at  $15^\circ$ , for an 80 per cent. acid, and then decreases again by further dilution. A detailed table for the calculation of the composition of aqueous acetic acid from the specific gravity is given in the section on "Organic Preparations" (Vol. III.).

Rüdorff recommends the determination of the temperature of solidification for the estimation of the composition of more concentrated acetic acids, and gives the following table:—

100 parts of Acetic Acid are mixed with	100 parts of the mixture contain	Temperature of Solidification.
0.0 Water	0.0 Water	+ $16^\circ.7$
0.5 "	0.497 "	+ $15^\circ.65$
1.0 "	0.980 "	+ $14^\circ.8$
1.5 "	1.477 "	+ $14^\circ.0$
2.0 "	1.961 "	+ $13^\circ.25$
3.0 "	2.912 "	+ $11^\circ.95$
4.0 "	3.846 "	+ $10^\circ.5$
5.0 "	4.761 "	+ $9^\circ.4$
6.0 "	5.660 "	+ $8^\circ.2$
7.0 "	6.542 "	+ $7^\circ.1$
8.0 "	7.407 "	+ $6^\circ.25$
9.0 "	8.257 "	+ $5^\circ.3$
10.0 "	9.090 "	+ $4^\circ.3$
11.0 "	9.910 "	+ $3^\circ.6$
12.0 "	10.774 "	+ $2^\circ.7$
15.0 "	13.043 "	- $0^\circ.2$
18.0 "	15.324 "	- $2^\circ.6$
21.0 "	17.855 "	- $5^\circ.1$
24.0 "	19.854 "	- $7^\circ.4$

In the colour industry, so-called glacial acetic acid (95 to 99 per cent. of acid) and also a more dilute acetic acid (35 to 50 per cent. of acid) are used. The most accurate method of estimating the content of acetic acid is titration with  $N/1$  sodium hydroxide, using phenolphthalein as indicator.

Crude acetic acid usually contains empyreumatic impurities, which can be detected by their odour after dilution, or, still better, after neutralisation. In the case of the more dilute acids, it is customary not to require a too stringent specification with regard to these impurities; 50 c.c. of the acid, after being evaporated to dryness for one and a half hours on a sand-bath, ought to leave only a very slight residue.

Greater purity is usually required of glacial acetic acid. It ought to have no, or only a very slight, empyreumatic odour after neutralisation, and should not decolorise a few drops of potassium permanganate immediately after their addition. Sulphurous acid, which is occasionally present, is detected by the decolorisation of iodide-starch paste, and also by the precipitation of sulphur, which occurs when the acid is mixed with a clear solution of hydrogen sulphide.

Glacial acetic acid is used in the colour industry mostly as a solvent, for the preparation of acetyl derivatives, etc. Dilute acetic acid is chiefly used for the weak acidification or the neutralisation of liquids when an excess of a mineral acid is not permissible.

### 9. Oxalic Acid, $C_2H_2O_4 \cdot 2H_2O$ .

The acid melts slightly above  $100^\circ$  in its water of crystallisation. It dissolves in fifteen parts of cold water, and much more readily in hot water or in alcohol. The anhydrous acid sublimes without decomposition when it is heated carefully to a temperature not exceeding  $150^\circ$ , but decomposes by rapid heating into carbon dioxide, carbon monoxide, formic acid, and water. The sodium salt is considerably less soluble than the potassium salt. Sodium hydrogen oxalate is precipitated by the addition of oxalic acid to a saturated solution of sodium chloride.

The commercial product is usually fairly pure, and contains at most small quantities of the alkali or the calcium salts, which are detected by the residue of ash.

Titration by  $N/1$  alkali hydroxide is the most convenient and accurate method for its examination. Oxalic acid can also be estimated very exactly by titration with potassium permanganate and sulphuric acid.

In the colour industry, oxalic acid is used chiefly in the preparation of rosolic acid, and of salts (malachite green). In dyeing, it is employed frequently for the preparation of acid mordants. For the latter purpose, and also for its recovery from the above processes, the following table,



compiled by Franz, giving the sp. gr. at 15° of aqueous solutions of oxalic acid, is of use:—

Spec. Grav. at 15°.	Amount of $C_2H_2O_4 \cdot 2H_2O$ .	Spec. Grav. at 15°.	Amount of $C_2H_2O_4 \cdot 2H_2O$ .
1·0032	1 per cent.	1·0226	8 per cent.
1·0064	2 "	1·0248	9 "
1·0096	3 "	1·0271	10 "
1·0128	4 "	1·0289	11 "
1·0160	5 "	1·0309	12 "
1·0182	6 "	1·0320	12·6 "
1·0204	7 "		

### 10. Formaldehyde, $CH_2O$ .

The technical product consists of a 40 per cent. solution of formaldehyde.

In order to prepare it, air is passed through wood spirit, warmed to 40° to 50°, and then over a moderately heated cylinder of coarse copper gauze. Aqueous formaldehyde has a pungent odour, reduces ammoniacal solutions of silver salts with the formation of a mirror, and yields crystals of trithioformaldehyde with hydrogen sulphide. When warmed with moderately dilute sodium hydroxide, formaldehyde is decomposed into formic acid and methyl alcohol. It combines readily with dilute ammonium hydroxide to form hexamethylene-tetramine. By keeping, a solution of formaldehyde yields the polymeric trioxymethylene,  $(CH_2O)_3$ , which, once deposited from the solution, is insoluble in water, alcohol, or ether.

The following reactions can be used for the quantitative analysis of formaldehyde:<sup>1</sup>—

1. It forms a silver mirror by warming with an ammoniacal solution of a silver salt.

2. 0·5 c.c. of dimethylaniline is added to 1 c.c. of formaldehyde solution and 10 c.c. of water, and the mixture is acidified with dilute sulphuric acid and well shaken. After being made alkaline with sodium hydroxide, the solution is boiled until the odour of dimethylaniline is not perceptible. The resulting tetramethyldiaminodiphenylmethane is collected on a filter, washed, and treated in a small porcelain basin with acetic acid and then with some finely powdered lead peroxide. A blue coloration is developed.

3. About 20 c.c. of the liquid to be tested for formaldehyde are treated with 20 c.c. of an aqueous solution of aniline (3 g. of aniline per 1 litre of water), and neutralised. According to the amount of aldehyde present, a white precipitate or a slight turbidity, frequently

<sup>1</sup> Cf. also B. M. Pilhashy, *J. Amer. Chem. Soc.*, 1900, 22, 132.

formed only after keeping for a few days, of anhydroformaldehyde-aniline is produced.

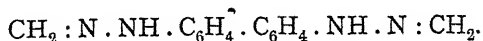
4. Since formaldoxime in aqueous solution is readily decomposed on boiling, into water and hydrogen cyanide,<sup>1</sup> hydroxylamine is a very sensitive reagent for the detection of formaldehyde. The solution to be tested is boiled with an aqueous solution of a hydroxylamine salt (obviously the hydrochloride is not applicable), and then examined for hydrogen cyanide.<sup>2</sup>

5. Lebbin<sup>3</sup> employs as a reagent a solution of the sodium derivative of resorcinol containing 40 to 50 per cent. of sodium hydroxide and 5 per cent. of resorcinol. Equal volumes of this solution and the aqueous liquid under examination (which must be free from coloured substances and albumins) are heated to boiling in a test tube and maintained so for a short time (about half a minute). Even in the presence of very small quantities of formaldehyde a distinct reddening is observable. The test will detect 0.2 to 0.1 part in a million.

6. B. A. van Ketel<sup>4</sup> states that when a solution of formaldehyde (about 35 per cent.) is poured on concentrated sulphuric acid, a white precipitate is formed within three minutes at the junction of the two liquids, which extends throughout the solution of formaldehyde, so that after some hours the whole formaldehyde solution is filled with a white crystalline mass. When a less concentrated solution is used, the reaction occurs distinctly more slowly. The resulting white substance is insoluble in water and is probably a polymeride of formaldehyde; on boiling with dilute sulphuric acid it evolves formaldehyde vapour.

7. *p*-Nitrophenylhydrazine is also suitable for the detection of formaldehyde.<sup>5</sup> Even a very dilute solution of formaldehyde, when treated with a small quantity of an aqueous solution of *p*-nitrophenylhydrazine hydrochloride, yields after a short time, or on warming, a precipitate of formaldehyde-*p*-nitrophenylhydrazone, which crystallises from benzene in yellow needles melting at 181°—182°.

8. C. Neuberg<sup>6</sup> detects formaldehyde by means of 4:4'-dihydrazinodiphenyl hydrochloride. Aqueous solutions of the latter and formaldehyde yield, after a short time at the ordinary temperature, instantly on warming to 50° to 60°, a flocculent, yellow precipitate which has the composition:—



This substance is formed in moderately dilute solutions. Solutions of formaldehyde (1 : 5000) are instantly coloured pale yellow by warming

<sup>1</sup> Scholl, *Ber.*, 1891, 24, 576.

<sup>2</sup> A. Brochet and R. Cambier, *Comptes rend.*, 1895, 120, 449.

<sup>3</sup> *Pharm. Zeit.*, 1897, 42, 18.

<sup>4</sup> *Pharm. Weekblad.*, 1894, 31, No. 49; *Jahresber. d. Pharm.*, 1895, 30, 275.

<sup>5</sup> E. Bamberger, *Ber.*, 1899, 32, 1207.

<sup>6</sup> *Ber.*, 1899, 32, 1961.

with a few drops of a solution of dihydrazinodiphenyl hydrochloride; the formation of a crystalline precipitate occurs only after a few minutes. The test is less trustworthy at dilutions of 1 : 8000. Although it is not so sensitive as A. Jorissen's phloroglucinol test<sup>1</sup> or Lebbin's resorcinol test (above), it has the advantage over these of being absolutely conclusive. The colorations<sup>c</sup> developed in the phloroglucinol and the resorcinol tests are produced by furfural in a similar manner. Moreover, it is not even necessary to use the purified dihydrazinodiphenyl hydrochloride. A little benzidine on the end of a spatula is dissolved in hydrochloric acid in a test tube and the cold solution is treated with sodium nitrite, whilst the tube is kept cool by running water. The diazo chloride is added to a solution of stannous chloride in concentrated hydrochloric acid; after a short time it is boiled with a little animal charcoal. The clear filtrate contains sufficient dihydrazinodiphenyl hydrochloride to give the test; the formaldehyde compound, however, often has an orange red shade (due to the presence of tin compounds?).

9. Romijn<sup>2</sup> gives a microscopic method for the detection of formaldehyde.

10. Feder's test<sup>3</sup> is as follows:—Twenty grams of mercuric chloride are dissolved in water and made up to a litre; 100 g. of sodium sulphite and 80 g. of sodium hydroxide are dissolved in water and made up to a litre. Equal quantities of these two solutions are mixed previously to the test, the sulphite solution being added rapidly, with stirring, to the mercury solution. 0.2 mg. of formaldehyde gives a distinct turbidity with this solution in a few seconds, whilst 0.05 mg. gives a perceptible reaction after one to two minutes. The amount of aldehyde in a solution can be determined from the weight of metallic mercury produced, 200 mg. of mercury being equivalent to 30 mg. of formaldehyde.

11. Gabutti<sup>4</sup> finds that when carbazole is treated with concentrated sulphuric acid in presence of a small quantity of formaldehyde, a blue coloration is produced, and in presence of larger quantities, a bluish green precipitate. This test is capable of detecting one part of formaldehyde in ten thousand in either aqueous or alcoholic solutions; the coloration resists the action of alkalis, but not of ammonia. The carbazole, and also the solution to be tested, must be free from nitric acid, nitrates, or other oxidising agents which give a colour reaction with carbazole alone.

<sup>1</sup> *J. Pharm. Chim.*, 1897, 167; *Z. angew. Chem.*, 1898, 11, 328.

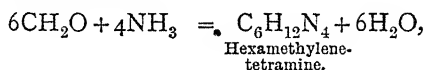
<sup>2</sup> *Pharm. Zeit.*, 1895, 40, 407.

<sup>3</sup> *Arch. Pharm.*, 1907, 245, 25.

<sup>4</sup> *Boll. Chim. Farm.*, 1907, 46, 349.

# Quantitative Estimation of Aqueous Solutions of Formaldehyde.<sup>1</sup>

1. The aqueous formaldehyde under examination is shaken with calcium carbonate, and 5 c.c. of the clear supernatant liquid are treated with 50 c.c. of *N*/1 ammonium hydroxide and kept for a day at the ordinary temperature in a closed vessel. The excess of the ammonium hydroxide is titrated with *N*/1 hydrochloric acid, using litmus as indicator. From the equation,



it is evident that the amount of ammonium hydroxide added is capable of reacting with 2.4 g. of formaldehyde, corresponding with a 48 per cent. solution of the aldehyde. For every c.c. of hydrochloric acid used in the titration, 0.048 g. of formaldehyde must be subtracted. If *n* c.c. of *N*/1 hydrochloric acid are used, the percentage of formaldehyde in the solution under examination is  $48 - n \times 0.96$ .<sup>2</sup>

If methyl orange is used as the indicator in the titration, it changes its colour completely only after the feebly basic hexamethylenetetramine, as well as the free ammonium hydroxide, has been converted into the hydrochloride. With the quantities stated above, the percentage of formaldehyde in the solution is, therefore,  $64 - n \times 1.28$ , where *n* is the number of c.c. of the hydrochloric acid used.<sup>3</sup>

A. Trillat<sup>4</sup> converts the formaldehyde into hexamethylenetetramine by a measured volume of ammonium hydroxide, distils the excess of the latter, and titrates it in the distillate.

M. Klar<sup>5</sup> uses the following method:—Sixty c.c. of *N*/1 ammonium hydroxide (=1.0200 g.  $\text{NH}_3$ ), previously well shaken, are placed in a normal 250 c.c. flask provided with an accurately fitting glass stopper, and 5 c.c. of the formaldehyde solution are then added. The flask is shaken and set aside for three to four hours. After this time it is shaken again, in order to dissolve the gaseous ammonia above the liquid. The stopper is raised carefully, 20 c.c. of *N*/1 acid are run in, and the solution is made up to 250 c.c. with water. The excess of the acid in portions of this solution is titrated by *N*/1, or, better, *N*/10 sodium hydroxide, using one or at most two drops of rosolic acid (or litmus) as indicator; the requisite number of c.c. multiplied by ten, gives the number of c.c. of *N*/1 sodium hydroxide required for the back titration, from which

<sup>1</sup> Cf. also Clowes, *Ber.*, 1899, **32**, 2841; J. Wolff, *Z. Unters. Nahr. u. Genussm.*, 1900, **3**, 87.

<sup>2</sup> Legler, *Ber.*, 1883, **16**, 1333; Eschweiler, *Ber.*, 1889, **22**, 1929; *Annalen*, 1890, **258**, 97.

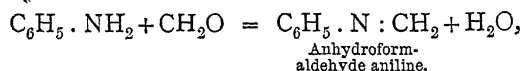
<sup>3</sup> Lösekann, *Ber.*, 1889, **22**, 1565.

<sup>4</sup> *Comptes rend.*, 1893, **116**, 291.

<sup>5</sup> *Pharm. Zeit.*, 1895, **40**, 438.

the percentage of formaldehyde is easily calculated. The titration is performed best in a small white porcelain basin, in which the change of colour of the indicator can be more sharply detected than in a beaker. Formaldehyde is seldom neutral, but usually has a slightly acid reaction. It is therefore also advisable to determine the acidity, in a second experiment, with *N*/1 sodium hydroxide and phenolphthalein, and to subtract the amount from the preceding result. The advantages of this method are the following:—a perfectly definite amount of ammonium hydroxide is used, only traces of ammonia are lost, and very much smaller volumes of liquid are titrated, in consequence of which only a trace of the indicator is necessary and the end-point is very much sharper.<sup>1</sup>

2. An aqueous solution of 3 g. of aniline in 1 litre of distilled water is continuously shaken and treated, drop by drop, with 2 c.c. of the formaldehyde solution to be tested. After forty-eight hours the precipitate is collected on a tared filter, dried at 40°, and weighed (an excess of aniline must be present in the filtrate). From the equation,



the percentage of formaldehyde in the solution can be calculated.<sup>2</sup>

M. Klar<sup>3</sup> utilises the formation of anhydroformaldehyde-aniline in a volumetric method, which, however, has no advantage over the ammonium hydroxide method.

The number of c.c. of *N*/10 hydrochloric acid required to neutralise 10 c.c. of a solution of 3 g. of the purest aniline in 1 litre of water is first determined. For this purpose, 10 c.c. of the solution are placed in a beaker, a few drops of Congo-red solution (1 : 1000) are added, and *N*/10 hydrochloric acid is run in, with stirring, until the red colour is changed to a violet strongly tinged with blue. This point is recognised by the fact that a further slight addition no longer changes the colour, and that a pure blue is obtained only with a much greater excess (Congo-red paper may also be used). The actual amount of aniline in the solution is calculated from the volume of acid used; 1 c.c. of *N*/10 hydrochloric acid represents 0.0093 g. of aniline.

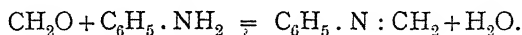
Four hundred c.c. of the titrated aniline solution are placed in a standard 500 c.c. flask, which is shaken while 1 c.c. of the formaldehyde solution under examination is added, drop by drop, from a burette; the flask is then filled to the mark. After some time, an aliquot portion is filtered through a dry filter into a dry flask and the excess of aniline in 50 c.c. of the filtrate is determined by *N*/10 hydrochloric acid, exactly as described above. The difference

<sup>1</sup> Cf. also Th. Salzer, *Pharm. Zeit.*, 1895, 40, 157.

<sup>2</sup> Trillat, *Comptes rend.*, 1893, 116, 891.

<sup>3</sup> *Pharm. Zeit.*, 1895, 40, 548.

between the total excess and the amount of aniline originally present represents the quantity of aniline which has reacted with the formaldehyde. The percentage of formaldehyde is easily calculated therefrom:—

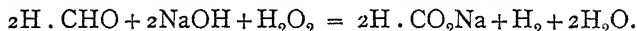


3. O. Blank and H. Finkenbeiner<sup>1</sup> state that the ammonium hydroxide method gives inaccurate results; in solutions containing 20 to 40 per cent. of formaldehyde, the result is about 1.5 per cent. too low. They have therefore elaborated a new method, in which the formaldehyde is oxidised to formic acid by hydrogen peroxide in alkaline solution and the excess of the alkali is titrated.

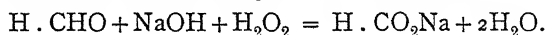
Three grams of the formaldehyde solution (or 1 g. of solid formaldehyde) are weighed in a weighing-bottle and introduced into 25 c.c. of *N*/2 sodium hydroxide (30 c.c. are taken for solutions stronger than 45 per cent.), contained in a tall Erlenmeyer flask. Immediately afterwards, 50 c.c. of pure 2.5 to 3 per cent. hydrogen peroxide are added slowly (in about 3 minutes) through a funnel to prevent splashing. (The hydrogen peroxide must be tested for acidity, for which an allowance must be made in the calculation.) After remaining for two to three minutes, the funnel is rinsed with water (from which, in accurate estimations, the carbon dioxide has been completely expelled by boiling), and the excess of sodium hydroxide is titrated with *N*/2 sulphuric acid. The indicator is a tincture of litmus. (When the tincture is being prepared, the reddish violet colouring matter must be extracted by alcohol, since otherwise the end-point is not sharp.) When solutions weaker than 30 per cent. are being estimated, an interval of about ten minutes after the addition of the hydrogen peroxide must be allowed for the completion of the reaction.

The percentage of formaldehyde is obtained directly by multiplying the number of c.c. of sodium hydroxide used by two when 3 g. of formaldehyde are employed, or by six when 1 g. of solid formaldehyde is taken.

A considerable evolution of heat and violent foaming accompany the reaction, which occurs according to the equation:—



Probably the following reaction also takes place:—



An alternative method of carrying out this process is described by Frankforter and West.<sup>2</sup>

The secondary reaction, indicated by the above equation, leads, according to Haywood and B. H. Smith,<sup>3</sup> occasionally to incorrect

<sup>1</sup> *Ber.*, 1898, 31, 2979.

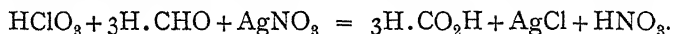
<sup>2</sup> *J. Amer. Chem. Soc.*, 1905, 27, 714.

<sup>3</sup> *Ibid.*, 1905, 27, 1183.

results. They give the following method of performing the test. Fifty c.c. of *N*/1 sodium hydroxide solution are mixed in a flask with 50 c.c. of pure 3 per cent. hydrogen peroxide solution, and then 3 c.c. of the formaldehyde solution under examination (the specific gravity of which has been previously determined) are added from a pipette, the point of which almost reaches the liquid in the flask. A funnel is placed in the neck of the flask, and the whole is heated on the steam-bath for five minutes, with occasional shaking. The funnel is then rinsed with distilled water, the flask cooled to the ordinary temperature, and the excess of sodium hydroxide titrated with *N*/1 acid, using litmus as indicator.

W. Fresenius and L. Grünhut<sup>1</sup> recommend the following modifications:—Twenty-five to thirty c.c. of *N*/2 sodium hydroxide (free from carbonate) are run from a burette into a 500 c.c. Erlenmeyer flask. About 3 g. of the formaldehyde solution are weighed in a cylindrical weighing-tube with a well-ground stopper. The tube is opened and stood upright on the bottom of the flask without spilling any of its contents. The aldehyde and the alkali are then mixed by tilting and rotating the flask. At this point 50 c.c. of 3 per cent. hydrogen peroxide are immediately added through a funnel at such a rate that the whole is introduced in three minutes. After two to three minutes, or ten minutes in the case of a sample containing less than 30 volumes per cent., the funnel and the walls of the flask are washed with water (free from carbon dioxide), and the excess of the alkali is titrated by *N*/1 sulphuric acid, using litmus or azolitmin as indicator. Paraformaldehyde can be estimated in the same way, but not trioxymethylene.

4. Formaldehyde reduces free chloric acid, but not chlorates.<sup>2</sup> The free chloric acid is not converted immediately into hydrochloric acid, but yields at first lower oxyacids, and then by further decomposition chlorine is generated, which reacts with the formic acid, simultaneously produced, to form carbon dioxide and hydrochloric acid. In the presence of a silver salt, however, the reduction proceeds thus:—



By further experiments, Grützner showed that one molecule of potassium chloride or of silver chloride is produced from one molecule of potassium chlorate and three molecules of formaldehyde.

The estimation is performed in the following way:—Approximately 1 g. of potassium chlorate is dissolved in 20 to 30 g. of water in a glass-stoppered flask, and then 50 c.c. of *N*/10 silver nitrate, 5 c.c. of the formaldehyde solution, and a little nitric acid are added. Parchment

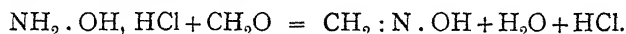
<sup>1</sup> *Z. anal. Chem.*, 1905, 44, 13; *J. Chem. Soc.*, 1905, 88, ii., 211.

<sup>2</sup> Grützner, *Arch. Pharm.*, 1896, 234, 634.

paper is bound over the flask, which is then heated, with occasional shaking, for half an hour in a lukewarm water-bath. There is no necessity to remove the silver chloride formed, so, after cooling, the excess of the silver is titrated with *N*/10 ammonium thiocyanate, using ferric alum as indicator; 1 c.c. of *N*/10 silver nitrate represents the ten-thousandth part of three molecules of formaldehyde, *i.e.*, 0.0090 g. of formaldehyde.

The analytical results can be controlled gravimetrically by weighing the separated silver chloride.

5. Formaldehyde reacts with a solution of hydroxylamine hydrochloride according to the equation:



A. Brochet and R. Cambier<sup>1</sup> employ this reaction in a volumetric method in which the indicator is methyl orange, which has a neutral reaction towards hydroxylamine hydrochloride.

6. Analogously to the Nessler reaction for ammonia in water, a colorimetric estimation<sup>2</sup> of formaldehyde at dilutions of from 1:100,000 to 1:1,000,000 can be made by means of a solution of the sodium derivative of resorcinol (see p. 899 for the preparation). Since stable turbidities are not produced at very great dilutions, the heating of all of the standard solutions with the resorcinol solution must be done simultaneously. Five c.c. of the resorcinol solution and of the liquids under examination are placed in testing-glasses of equal thickness, which are shaken, placed altogether in the same beaker of glycerol, and heated.

7. A cold aqueous solution of pure dihydrazinodiphenyl hydrochloride (which has been recrystallised repeatedly and dissolves in water completely) is treated slowly and with continual stirring with the liquid containing the formaldehyde, and the mixture is warmed very gradually to 50° to 60° during the course of fifteen minutes. The precipitate is allowed to settle, and is then collected, without further delay, best on a Gooch crucible at the pump, washed first with hot water, and finally with alcohol and absolute ether, and dried in the oven at 90°. During the drying, the precipitate must retain its clear yellow colour. Only under this condition and at suitable dilutions are accurate results obtained. The dilution of the solution must be such that it contains one to two parts of formaldehyde to one-thousand parts of water. (The composition of the hydrazone is given on p. 899.)

The method can be advantageously used where volumetric methods fail, namely, in the estimation of formaldehyde in mixtures containing other aldehydes, ketones, or acids. In this case, before the addition of the dihydrazinodiphenyl hydrochloride, the liquid under examination

<sup>1</sup> *Comptes rend.*, 1895, 120, 449.

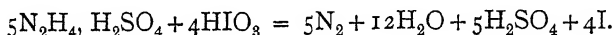
<sup>2</sup> Lebbin, *Pharm. Zeit.*, 1897, 42, 18.



is treated, according to the amount of the other constituents, with one to two volumes of absolute ethyl alcohol, or better, methyl alcohol; the estimation is otherwise performed as described for pure formaldehyde solutions.

When the solution does not contain substances, other than the formaldehyde, which attack the hydrazine hydrochloride, iodine, or sodium thiosulphate, the aldehyde can be estimated volumetrically by determining, by E. von Meyer's iodine and thiosulphate method,<sup>1</sup> the excess of the hydrazine in the filtrate, after the removal of the precipitated methylenediphenylenedihydrazone. Very largely diluted solutions, however, must be used, and on this account Blank and Finkenbeiner's method (p. 903) is preferable.

8. E. Riegler's gas-volumetric method:<sup>2</sup>—When hydrazine sulphate reacts with a solution of iodic acid, the whole of the nitrogen is liberated:



Formaldehyde and hydrazine yield a hydrazone which is decomposed by iodic acid only after some time. When a standard solution of hydrazine sulphate is decomposed, with and without the addition of formaldehyde, the quantity of the latter can be calculated from the difference of the volumes of nitrogen evolved, since 1 c.c. of nitrogen at 0° and 760 mm. represents 0.0027 g. of formaldehyde. The estimation is performed in the Knop-Wagner nitrometer. The solutions required are:

1 g. of hydrazine sulphate in 100 c.c. of water,  
and 5 g. of pure crystallised iodic acid in 50 c.c. of water.

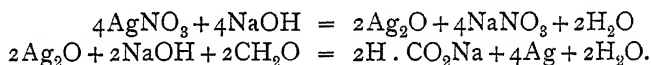
Twenty c.c. of the solution of hydrazine sulphate are transferred into the outer compartment of the generating vessel of the nitrometer by means of a pipette, and 20 c.c. of water are also added, whilst 5 c.c. of the solution of iodic acid are placed in the inner compartment. The generating vessel is then closed by a rubber stopper and immersed in the cooling cylinder, which contains cold water, until the stopper is just covered by the water. After an interval of ten minutes, the level of the water is exactly adjusted to the zero of the graduated tube, the glass stopcock is firmly inserted and turned so that the generating vessel is put into communication with the graduated tube. The generating vessel is then removed from the cooling cylinder and shaken vigorously for half a minute, whilst previously 20 c.c. of water have been allowed to flow through the pinch-cock. The generating vessel is replaced in the cooling cylinder, and after two minutes the volume of the liberated nitrogen is read. Twenty c.c. of the

<sup>1</sup> *J. prakt. Chem.*, 1887 [ii.], 36, 115.

<sup>2</sup> *Z. anal. Chem.*, 1901, 40, 92; *J. Chem. Soc.*, 1901, 80, ii., 360.

solution of hydrazine sulphate are then measured accurately into a flask, and a known volume of the aqueous formaldehyde solution under examination (the known volume must not contain, at most, more than 0.08 g. of formaldehyde) is added, and the mixture is shaken and allowed to stand for fifteen minutes. The mixture is then transferred to the outer compartment of the generating vessel of the nitrometer. The flask is rinsed with distilled water, and so much of the rinsings is placed in the generating vessel that the volume of the rinsings, plus the volume of the aqueous formaldehyde taken, measure about 20 c.c. Five c.c. of the 10 per cent. iodic acid solution are transferred into the inner compartment by means of a pipette, and the estimation is continued as above.

9. L. Vanino<sup>1</sup> estimates formaldehyde in its solutions gravimetrically by silver nitrate. A precipitate of silver oxide is obtained by treating a solution of formaldehyde with silver nitrate and sodium hydroxide. By the addition of dilute acetic acid, the silver oxide is dissolved, whilst the precipitated silver remains unchanged. The reactions which occur are the following:—



For the estimation an aqueous solution of 2 g. of silver nitrate is treated with pure sodium hydroxide, free from chloride, until a strongly alkaline reaction is produced. Five c.c. of a solution of formaldehyde, prepared from 10 c.c. of commercial formalin and 100 c.c. of water, are at once added, with stirring, and the mixture is set aside in the dark. After about fifteen minutes, the clear supernatant liquid is poured through a tared filter and the precipitate is digested three or four times with approximately 5 per cent. acetic acid, brought on to the filter, washed with water (faintly acidified with acetic acid) until free from silver oxide, dried at 105°, and weighed.

10. The estimation of formaldehyde by potassium permanganate, according to H. M. Smith's method,<sup>2</sup> fails through the difficulty of detecting the end-point. L. Vanino and E. Zeitter<sup>3</sup> find that good results are obtained in a strong sulphuric acid solution by means of hydrogen peroxide. Thirty-five c.c. of *N*/5 potassium permanganate are placed in a vessel, best in a 250 c.c. flask fitted with a well-ground stopper, and are diluted with a previously prepared and cooled mixture of 30 g. of concentrated sulphuric acid and 50 g. of water. Into the mixture are dropped, slowly and with constant shaking, 5 c.c. of an approximately 1 per cent. formalin solution, previously prepared by diluting 10 c.c. of commercial formalin to

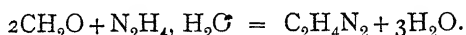
<sup>1</sup> *Z. anal. Chem.*, 1901, 40, 720.

<sup>2</sup> *Analyst*, 1896, 21, 148.

<sup>3</sup> *Z. anal. Chem.*, 1901, 40, 587.

400 c.c. The flask is then stoppered, set aside for ten minutes, and occasionally shaken. The excess of the potassium permanganate is titrated with approximately *N*/10 hydrogen peroxide which has been standardised by potassium permanganate. According to Grossmann and Aufrecht,<sup>1</sup> the mixture should be kept for one hour, otherwise too low results are obtained.

11. A new method<sup>2</sup> of estimating formaldehyde is based on Curtius and Pulvermacher's observation<sup>3</sup> that formaldehyde and hydrazine yield formalazine:



An excess of a solution of hydrazine hydrate, which has been standardised with *N*/10 sulphuric acid, is digested with the formaldehyde solution under examination, and the uncombined hydrazine hydrate is titrated with *N*/10 sulphuric acid, using methyl orange as indicator. In calculating the result, it must be remembered that 1 molecule of sulphuric acid combines with 2 molecules of hydrazine, forming the diammonium semisulphate  $(\text{N}_2\text{H}_4)_2\text{H}_2\text{SO}_4$ , not the diammonium sulphate  $(\text{N}_2\text{H}_4)\text{H}_2\text{SO}_4$ . Since the solution of hydrazine hydrate does not long retain its value, it must be titrated with *N*/10 sulphuric acid before each estimation, and its colour can be used as a guide in the back-titration.

12. The condensation product of formaldehyde and catechin is very suitable for the estimation of formaldehyde or conversely of catechin.<sup>4</sup> Twenty grams of catechin (air-dried, it contains 15 per cent. of water) are dissolved in 200 c.c. of hot water, treated with 1 c.c. of 5 per cent. hydrochloric acid and 30 c.c. of 40 per cent. formaldehyde solution, and digested on the water-bath for one hour. Almost concurrently with the addition of the formaldehyde, a flocculent, amorphous, nearly white precipitate is produced, which weighs 17 g. after being collected and dried in a vacuum.

Clauser is of opinion that the reaction ought to serve admirably for the estimation of formaldehyde and also of catechin.

13. C. Kleber recommends the following simple method for the estimation of formaldehyde and paraformaldehyde:—A concentrated solution of commercial sodium hydrogen sulphite is treated with sodium hydroxide until the odour of sulphur dioxide has completely disappeared, and is then diluted with water until 30 c.c. of the solution correspond exactly with 50 c.c. of *N*/1 sodium hydroxide, using phenolphthalein as indicator. Five c.c. of the formaldehyde solution, which generally has an acid reaction, are neutralised by sodium hydroxide, using phenolphthalein as indicator, and are then titrated with the preceding solution of sodium hydrogen

<sup>1</sup> *Ber.*, 1906, 39, 2455.

<sup>2</sup> *Chem. Zeit.*, 1902, 26, 701.

<sup>3</sup> A. Pfaff, *Ber.*, 1893, 26, 2360.

<sup>4</sup> R. Clauser, *Ber.*, 1903, 36, 106.

sulphite until the red colour again vanishes. Concentrated solutions, in consequence of a spontaneous development of heat, can be titrated readily, but weaker solutions require warming towards the end of the titration. For the dilutions given, the number of c.c. of the sulphite solution used represents the number of grams of formaldehyde in 100 volumes of the solution. In the case of paraformaldehyde, 2 g. of the substance are dissolved in a little water and titrated in the same way; 1 c.c. of the sodium hydrogen sulphite solution represents 0.05 g. of paraformaldehyde. The prepared solution of sodium hydrogen sulphite is serviceable so long as it does not smell too strongly of sulphur dioxide.<sup>1</sup>

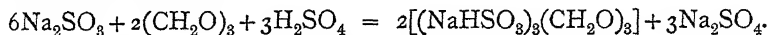
14. M. Ripper<sup>2</sup> describes the following volumetric method, which is generally used:—

An aqueous solution of the aldehyde is treated with an excess of a solution of an alkali hydrogen sulphite, in which the amount of sulphur dioxide has been previously determined by iodine. After a short time the whole of the aldehyde is combined with the hydrogen sulphite, which in this form is not oxidised by iodine. The residual sulphurous acid is titrated, and the amount of the aldehyde is calculated from the difference. An aqueous 0.5 per cent. solution of the aldehyde and a solution of 12 g. of potassium hydrogen sulphite per litre are the best to use, since with these concentrations reduction of the sulphuric acid by iodine during the titration need not be feared.

(The method is also applicable to acetaldehyde, benzaldehyde, etc.)

15. A. Seyewetz and Gibello<sup>3</sup> base a method of estimating formaldehyde and its polymerides on the following facts:—

Formaldehyde and sodium sulphite alone do not interact in the cold. By the addition of sulphuric acid to the solution, the sulphite is converted into the hydrogen sulphite and the sulphate, the former of which is at once absorbed by the formaldehyde. Since the formaldehyde sodium hydrogen sulphite compound has a neutral reaction towards phenolphthalein, the sulphuric acid does not decolorise this indicator until the whole of the formaldehyde has been converted into the additive compound. The reaction occurs, therefore, according to the following equation:—



The reaction is very suitable for the rapid titration of the polymerides of formaldehyde. For this purpose 20 c.c. of an approximately 20 per cent solution of sodium sulphite are titrated, using one drop of alcoholic 2 per cent. phenolphthalein as indicator, in order to ascertain the amount of standard acid required to neutralise the alkalinity of the sulphite solution. Then 0.5 to 0.7 g. of the trioxymethylene under

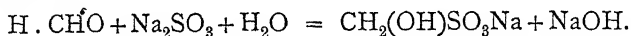
<sup>1</sup> *Pharm. Rev.*, 1904, **22**, 1894.

<sup>2</sup> *Monatsh.*, 1900, **21**, 1079.

<sup>3</sup> *Bull. Soc. Chim.*, 1904 [iii.], **31**, 691; *J. Chem. Soc.*, 1904, **86**, ii., 521.

examination is dissolved in 20 c.c. of the sulphite solution, which is again titrated. An excess of sodium sulphite is necessary to ensure the immediate formation of the bisulphite compound. It is advisable not to add more phenolphthalein than is just necessary.

16. G. Lemme<sup>1</sup> bases a method of estimating formaldehyde in solution on the reaction:—



The liberated sodium hydroxide is titrated by sulphuric acid.

17. W. Fresenius and L. Grünhut<sup>2</sup> employ Romijn's iodometric method<sup>3</sup> in the following way:—Twenty-five c.c. of the formaldehyde solution are weighed accurately in a tared weighing-bottle with a well-ground stopper, and are washed without loss into a 500 c.c. flask. The solution is made up to the mark, and 5 c.c. are accurately measured, into a bottle with a well-ground stopper. Thirty c.c. of *N*/1 sodium hydroxide, which need only be measured in a graduated cylinder, are rapidly added. About 50 c.c. of *N*/5 iodine are immediately run in from a burette with frequent shaking, until the liquid is deep yellow. The bottle is stoppered, well shaken for half a minute, and the contents acidified with 40 c.c. of *N*/1 sulphuric acid (measured in a graduated cylinder), and after a short time, during which the bottle is kept stoppered, the excess of iodine is titrated with *N*/10 sodium thiosulphate. Special attention must be given to the presence of any iodine in the potassium iodide used and of any nitrite in the alkali hydroxide. Hitherto, investigators have never troubled about acetone and ethyl alcohol—impurities in the formaldehyde solution which render the method inaccurate. Both would be detected by the iodoform reaction.

18. Feder's test (p. 900) can also be used for the quantitative estimation of formaldehyde. A similar test has been proposed by Orloff,<sup>4</sup> in which a solution of mercuric-potassium iodide is employed instead of the mercuric solution used by Feder.

After a comparative examination of the different methods of estimating formaldehyde, Bernhard H. Smith<sup>5</sup> arrives at the following conclusions:—

Blank and Finkenbeiner's method is specially suitable for concentrated solutions, and for such gives accurate results. It is important to wait a few minutes after the addition of the hydrogen peroxide, before back-titrating.

Legler's method gives rather lower results than the preceding

<sup>1</sup> *Chem. Zeit.*, 1903, 27, 896.    <sup>2</sup> *Z. Anal. Chem.*, 1905, 44, 13.    <sup>3</sup> *Ibid.*, 1897, 36, 18.

<sup>4</sup> *J. Russ. Phys. Chem. Soc.*, 1904, 36, 1311; *J. Soc. Chem. Ind.*, 1905, 24, 348.

<sup>5</sup> *J. Amer. Chem. Soc.*, 1903, 25, 1028; *Z. angew. Chem.*, 1904, 17, 303; see also Z. Peska, *Chem. Zeit.*, 1901, 25, 743; A. G. Craig, *J. Amer. Chem. Soc.*, 1901, 23, 638; O. Blank and H. Finkenbeiner, *Chem. Zeit.*, 1901, 25, 794; C. Wallnitz, *Z. angew. Chem.*, 1903, 16, 326.

method. The back-titration should be performed after twenty-four hours, using rosolic acid as indicator. The end-point of the titration is not sharp.

The gravimetric hexamethylenetetramine method is not practicable, since the hexamethylenetetramine loses weight continuously while drying.

The oxidation of formaldehyde by iodine, according to the methods of Romijn and others, gives good results for dilute formaldehyde solutions, and the same is true of the potassium cyanide method, by which even one part of formaldehyde in 100,000 parts of water can be estimated.

Volumetric methods with aniline solutions did not give any result, since the end-point of the titrations could not be detected.

Williams<sup>1</sup> has also made a study of the methods for the estimation of formaldehyde, and his conclusions are, in the main, the same as Smith's.

Formaldehyde is employed in the colour industry for the preparation of diphenylmethane derivatives (auramine), of triphenylmethane dyes (new magenta, formyl violet, Helvetia blue, aurintricarboxylic acid), and of a few dyes of the acridine series.

### Estimation of Methyl Alcohol in Formaldehyde.

1. Method of the Verein für chemische Industrie.<sup>2</sup> Ten grams of concentrated formaldehyde, containing 40 per cent. of the aldehyde, are weighed in a tared, 100 c.c. flask, which is then filled to the mark with distilled water. Five c.c. of this diluted solution are heated in a sealed tube at 140° for six hours with 100 c.c. of a solution of potassium bichromate, which contains 29.52 g. of potassium bichromate and 32 g. of concentrated sulphuric acid per litre. After cooling and diluting the liquid to 250 c.c., 25 c.c. are treated with potassium iodide and hydrochloric acid and titrated with *N*/10 sodium thiosulphate. Before titrating, the solution must be shaken for five minutes with the potassium iodide and hydrochloric acid.

*Example.*—Twenty-five c.c. of the diluted potassium bichromate solution required 15.3 c.c. of *N*/10 sodium thiosulphate, representing 0.0752 g. of potassium bichromate. Consequently, the whole solution (250 c.c.) contains 0.752 g. of potassium bichromate, since 100 c.c. of the potassium bichromate solution, containing 2.952 g. of potassium bichromate, were originally added. Therefore 2.2 g. of potassium bichromate have been used in oxidising formaldehyde, formic acid, and any methyl alcohol which is possibly present. The analysis of the aldehyde solution showed the presence of 40.3 per cent. of

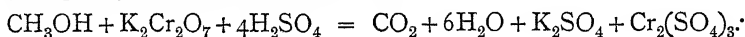
<sup>1</sup> *J. Amer. Chem. Soc.*, 1905, **27**, 596.

<sup>2</sup> *Z. anal. Chem.*, 1900, **39**, 62.

formaldehyde and 0.1 per cent. of formic acid, so that in the 5 c.c., corresponding with 0.5 g. of the formaldehyde solution, 0.2015 g. of formaldehyde and 0.0005 g. of formic acid are present.

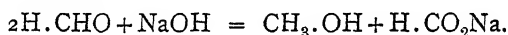
		Potassium bichromate.
0.2015 g. of formaldehyde requires for complete oxidation	.	1.32 g.
0.0005 g. of formic acid	„ „ „	0.001 g.
Total	.	<u>1.321 g.</u>

Consequently, 2.2 to 1.321 (=0.879 g.) of potassium bichromate have been used in oxidising methyl alcohol, the amount of which, therefore, is 0.0953 g., representing 19.06 per cent.



This process is carried out by Blank and Finkenbeiner<sup>1</sup> as follows:— One gram of the formaldehyde is weighed out, and is then added to a mixture of 50 c.c. of a *N*/2 solution of chromic acid and 20 c.c. of pure concentrated sulphuric acid. After standing for about twelve hours, or a shorter time if heat be employed, the liquid is diluted to 1 litre, and 50 c.c. are titrated with *N*/10 thiosulphate after the addition of a crystal of potassium iodide. The quantity of methyl alcohol is calculated as above.

2. Another method for the estimation of methyl alcohol depends on the well-known reaction:—



One hundred grams of the aldehyde are weighed into a strong, not too small, round-bottomed flask, which, after the addition of 700 g. of *N*/2 sodium hydroxide, is connected to an efficient upright water-condenser, above which is attached a spiral condenser cooled by ice. The flask is heated to boiling for two hours. When the condensers are not large and cold enough, a considerable loss is easily entailed, and low values for methyl alcohol are obtained. After the apparatus has cooled, the vertical condenser is removed and 300 to 400 c.c. of the liquid are distilled with efficient cooling. The amount of methyl alcohol in the distillate is ascertained by an accurate determination of the specific gravity, from which the percentage of methyl alcohol in the original aldehyde solution is calculated. The preceding equation shows that the aldehyde present is decomposed, and the distillate contains, therefore, first, methyl alcohol produced by the decomposition of formaldehyde, and secondly, methyl alcohol present as such in the aldehyde solution. The first amount, which is calculated from the known percentage of formaldehyde, is subtracted from the total amount of methyl alcohol, and the difference gives the amount of free methyl alcohol present in the aldehyde solution under examination.

<sup>1</sup> *Ber.*, 1906, 39, 1326.

The specific gravity of the distillate, which must be exact to the fourth decimal place, must be determined very accurately by a pyknometer, and exact tables must be used for the calculation. It is advisable to use the purest possible sodium hydroxide. Usually the results are fairly correct, but unfortunately are not absolutely trustworthy because in many cases the decomposition of the aldehyde not only proceeds according to the equation given above, but also yields other substances, sugar, etc., with the result that the amount of free methyl alcohol is too low; for example, only 18 per cent. instead of 20 per cent. The error must never be greater than this.

3. A third method depends on the condensation of the formaldehyde with a suitable substance, removal of the methyl alcohol by distillation, and a determination of the specific gravity of the distillate.<sup>1</sup> It is performed in the following way:—

Forty c.c. of water are heated to boiling in a small flask, and 110 g. of crystallised sodium sulphanilate (for products containing a low percentage of methyl alcohol, it is sufficient to use 90 g. of sodium sulphanilate and 35 c.c. of water) are added in small portions, and the mixture is again boiled until all is dissolved. The flask is cooled rapidly and the crystalline cake is coarsely broken by a glass rod. Exactly 20 c.c. of the formaldehyde solution under examination are then run in. The flask is closed by a cork and kept for three to four hours with occasional shaking. In order to save time, the flask may be placed on a water-bath, maintained at 35°—40°, whereby the reaction is completed in one and a half to two hours. After this time the odour of formaldehyde is inappreciable, the crystals of sodium sulphanilate have dissolved almost entirely, and the contents of the flask are fairly viscous.

(The condensation requires a considerably longer time when sodium sulphanilate is used directly, without being brought into a state of fine division in the way given above.)

The flask is then connected to a long tube-condenser by means of a delivery tube filled with beads, and its contents are distilled on a sand-bath, or, better, in an oil-bath (temperature 125° to 145°). Thirty to thirty-five c.c. are distilled over, the condenser is washed out with water, and the distillate and washings are made up to volume in a 50 c.c. flask. In order to avoid loss during the distillation, it is advisable to moisten the condenser and the receiver before distilling, since the first drops of the distillate are particularly rich in methyl alcohol. A very convenient form of condenser is that of Sauer and Göckel, which contains two tubes and can be connected air-tight to the receiver.

The density of the distillate is determined by a pyknometer,

<sup>1</sup> R. Gnehm and F. Kaufler, *Z. angew. Chem.*, 1904, 17, 673.



which should have a ground-in thermometer, since variations of the temperature from  $15^{\circ}$  cause great errors. The contents of the 50 c.c. flask are cooled in water at  $10^{\circ}$ – $12^{\circ}$ , and poured into the pyknometer, and the temperature is allowed to rise slowly to  $15^{\circ}$  by keeping the pyknometer in a moderately warm place. As soon as this temperature is attained the pyknometer is wiped with fibreless filter-paper, the cap is affixed, and the apparatus weighed after a short interval in the balance-case. The weights of the pyknometer, empty and filled with distilled water at  $15^{\circ}$ , will have been determined previously. Since the method is employed for technical purposes, the specific gravity given in the following table and referred to distilled water at  $15^{\circ}$ , have not been reduced to their values in vacuo. The values must be multiplied by 2.5, since the 20 c.c. have been diluted to 50 c.c. When ascertained under the preceding conditions—that is, without a thermostat and without those precautionary measures which are essential for an accurate determination—the specific gravity varies at most by 0.0001, and therefore, after multiplying by 2.5, the error is less than 0.2 per cent. The exact specific gravities of dilute methyl alcoholic solutions are given by Dittmar and Fawsitt<sup>1</sup> (cf. also p. 894), and confirm the values given below, calculated from the following equation:—

If  $P_o$  = weight of pyknometer, empty  
 $P_w$  =       "       "       with water at  $15^{\circ}$   
 $P$  =       "       "       the solution at  $15^{\circ}$

then the specific gravity is given by :

$$d_{15}^{15} = \frac{P - P_o}{P_w - P_o}$$

Grms. of Methyl Alcohol in 100 c.c.	$d_{15}^{15}$ calculated.	$d_{15}^{15}$ found.
0.2	0.99957	0.99962
0.4	0.99924	0.99923
0.6	0.99887	0.99887
0.8	0.99849	0.99849
0.99	0.99813	0.99808
1.19	0.99777	0.99772
1.59	0.99703	0.99697
1.99	0.99630	0.99638
2.13	0.99605	0.99609
2.38	0.99552	0.99549
3.57	0.99348	0.99352
4.77	0.99141	0.99140
6.36	0.98873	0.98873
7.95	0.98622	0.98622
8.92	0.98549	0.98546
9.54	0.98378	0.98379

<sup>1</sup> *Trans. Roy. Soc. Edinburgh*, 1889, 33, 509; cf. *J. Chem. Soc.*, 1889, 56, 578.

From a series of specific gravity determinations with mixtures of methyl alcohol and water containing 0 to 10 g. of methyl alcohol in 100 c.c. of the mixture, the following empirical formula is derived:—

$$d_{15}^{15} = 1 - 0.00189p + 0.00002p^2$$

where  $p$  represents the weight, in grams, of methyl alcohol in 100 c.c.

(The following table is calculated from the preceding formula. The last decimal figure is not absolutely trustworthy, as is also shown by the specimen analyses.)

$D_{15}^{15}$  of Dilute Solutions of Methyl Alcohol.

Grms. in 100 c.c.	$d_{15}^{15}$	Grms. in 100 c.c.	$d_{15}^{15}$	Grms. in 100 cc.	$d_{15}^{15}$
0.1	0.99981	3.5	0.99360	6.8	0.98805
0.2	0.99962	3.6	0.99343	6.9	0.98789
0.3	0.99943	3.7	0.99325	7.0	0.98773
0.4	0.99924	3.8	0.99308	7.1	0.98757
0.5	0.99905	3.9	0.99291	7.2	0.98741
0.6	0.99887	4.0	0.99273	7.3	0.98725
0.7	0.99868	4.1	0.99256	7.4	0.98709
0.8	0.99849	4.2	0.99239	7.5	0.98693
0.9	0.99831	4.3	0.99221	7.6	0.98677
1.0	0.99812	4.4	0.99204	7.7	0.98661
1.1	0.99793	4.5	0.99187	7.8	0.98646
1.2	0.99775	4.6	0.99170	7.9	0.98630
1.3	0.99756	4.7	0.99153	8.0	0.98614
1.4	0.99738	4.8	0.99136	8.1	0.98599
1.5	0.99720	4.9	0.99119	8.2	0.98583
1.6	0.99701	5.0	0.99102	8.3	0.98568
1.7	0.99683	5.1	0.99085	8.4	0.98552
1.8	0.99665	5.2	0.99069	8.5	0.98536
1.9	0.99647	5.3	0.99052	8.6	0.98521
2.0	0.99628	5.4	0.99035	8.7	0.98505
2.1	0.99610	5.5	0.99018	8.8	0.98490
2.2	0.99592	5.6	0.99002	8.9	0.98475
2.3	0.99574	5.7	0.98985	9.0	0.98460
2.4	0.99556	5.8	0.98968	9.1	0.98445
2.5	0.99538	5.9	0.98952	9.2	0.98430
2.6	0.99520	6.0	0.98936	9.3	0.98415
2.7	0.99502	6.1	0.98919	9.4	0.98400
2.8	0.99484	6.2	0.98903	9.5	0.98384
2.9	0.99466	6.3	0.98886	9.6	0.98369
3.0	0.99449	6.4	0.98870	9.7	0.98354
3.1	0.99431	6.5	0.98853	9.8	0.98340
3.2	0.99413	6.6	0.98837	9.9	0.98325
3.3	0.99396	6.7	0.98821	10.0	0.98310
3.4	0.99378				

It remains to be stated that very small quantities of reducing substances can always be detected by ammoniacal silver nitrate solution in the distillates, which retain a peculiar odour quite different from that of formaldehyde. That these substances are present only in minute traces is proved by titrating the distillates from aldehyde

solutions, which are practically free from methyl alcohol, with potassium permanganate. Since, however, they are apparently heavier than water, their presence introduces a small error, causing the results to be too low by about 0.5 to 0.6 g. in 100 c.c. of solution.

4. H. Bamberger<sup>1</sup> recommends the following method, which should give somewhat higher and more correct results:—

Fifty c.c. of the aldehyde are treated with 140 c.c. of a solution of sodium hydrogen sulphite containing 1 g.-mol. in 200 c.c. (therefore a small excess). The flask is closed by a tightly-fitting cork and kept for four to five hours until the hydroxymethylene-sulphonic acid has been formed. When the condensation is complete, the mixture is exactly neutralised by sodium hydroxide. The end-point is found by "spotting" on brilliant-yellow paper or phenolphthalein paper, since the addition of alcoholic phenolphthalein is inadmissible. The first drop of the alkali in excess is thus accurately shown. If the solution has been accidentally rendered alkaline, the error can be rectified without trouble by the addition of dilute sulphuric acid or of the bisulphite solution until only a faint alkaline reaction is produced. After neutralising, the flask is connected by a delivery tube to a condenser, and by distillation from an oil-bath about 75 c.c. of distillate are collected in a 100 c.c. measuring flask. After filling the flask to the mark, the specific gravity at 15° is determined by Mohr's balance.

5. Zeisel's iodide process<sup>2</sup> is suitable for the estimation of methyl alcohol in commercial formaldehyde.<sup>3</sup>

Five c.c. of formalin are diluted with 100 c.c. of water, made strongly alkaline with ammonium hydroxide, and distilled until 50 c.c. have been collected in a 100 c.c. flask. The contents of the flask are faintly acidified with pure acetic acid, and made up to the mark; 5 c.c. of the solution are submitted to the iodide process.

$\text{AgI} \times 54.57$  represents g. of methyl alcohol in 100 c.c. of formalin.

It is not yet decided which of the proposed methods gives the most accurate results, but H. Bamberger's method is generally preferred from its practicability and cheapness.<sup>4</sup>

## 11. Formic Acid, $\text{H} \cdot \text{CO}_2\text{H}$ .

Anhydrous formic acid, which is now a commercial product, is prepared by treating sodium formate with sulphuric or hydrofluoric acids or sodium hydrogen sulphate, and distilling. The sodium salt is made by the action of carbon monoxide on powdered sodium hydroxide

<sup>1</sup> *Z. angew. Chem.*, 1904, 17, 1246.

<sup>2</sup> *Z. anal. Chem.*, 1904, 43, 387.

<sup>3</sup> *Ibid.*, 1904, 43, 401.

<sup>4</sup> M. J. Stritar, R. Gnehm, and F. Kaufler, *Z. angew. Chem.*, 1905, 18, 93.

under pressure. Pure anhydrous formic acid melts at  $8^{\circ}\cdot6$ , boils at  $100^{\circ}\cdot6$  under a pressure of 760 mm., and has a sp. gr. of 1.22 at  $20^{\circ}$ . Formic acid may be estimated by the following methods:—

1. Oxidation by sodium hypobromite:<sup>1</sup>—A measured volume of standard hypobromite solution (made by dissolving 15 g. of sodium hydroxide in 450 c.c. of water, cooling, adding 5 c.c. of bromine, and making up to 500 c.c.) is diluted to 70 to 100 c.c. in a stoppered flask, and the formic acid added in such a quantity that about half the hypobromite remains in excess. Dilute hydrochloric acid is dropped in from a pipette until the yellow colour of bromine becomes permanent. The solution is then kept for thirty minutes in the dark, after which about 1 g. of potassium iodide and 10 to 20 c.c. of dilute hydrochloric acid are added, and the liberated iodine titrated with  $N/10$  thiosulphate solution. The difference between the initial and final iodine values gives the amount of hypobromite used. One c.c. of  $N/10$  thiosulphate corresponds with 0.0023 g. of formic acid.

2. Oxidation by potassium permanganate:<sup>2</sup>—A measured volume of formic acid (or formate) solution, containing not more than 1 per cent. of the acid, is placed in a stoppered flask, an excess of  $N/10$  permanganate solution and 0.5 g. of anhydrous sodium carbonate are added, and the mixture is heated in a water-bath for thirty minutes. After cooling, 75 c.c. of water, 25 c.c. of dilute sulphuric acid, and 2 g. of potassium iodide are added, and the liberated iodine is titrated with thiosulphate solution.<sup>3</sup>

3. Oxidation by mercuric chloride:<sup>4</sup>—To the solution containing 0.2 to 1 g. of formic acid, as a solution salt, in 1 litre, are added 7.5 to 15 g. of mercuric chloride, dissolved in 100 to 203 c.c. of hot water; the liquid is stirred and heated on a water-bath, until the precipitated mercurous chloride has settled, and then sodium hydroxide is added to the hot liquid, until a brownish precipitate of mercuric oxide becomes permanent. The liquid is again heated on the water-bath, and after the precipitate has completely settled, the neutralising is repeated. The precipitate is once more made to settle by heating on the water-bath, and then 20 c.c. of strong hydrochloric acid are added and the heating continued for an hour. The whole process of reduction takes about two and a half hours. The precipitate is collected in a Gooch crucible, well washed with hot water, dried for six to eight hours in the steam oven and then for several hours in a vacuum desiccator; its weight, multiplied by the factor 0.097726, gives the corresponding weight of formic acid. When it is not possible to carry out the determination

<sup>1</sup> E. Rupp, *Arch. Pharm.*, 1905, 243, 69.

<sup>2</sup> E. Rupp, *Z. anal. Chem.*, 1906, 45, 687.

<sup>3</sup> Cf. Grossmann and Aufrecht, *Ber.*, 1906, 39, 2455.

<sup>4</sup> H. Franzen and G. Greve, *J. prakt. Chem.*, 1909, [ii.], 80, 368.

directly on the solution to be examined, accurate results may be obtained by first distilling the formic acid in a current of steam and in the presence of phosphoric acid, using the neutralised distillate for the estimation.

### 12. Carbonyl Chloride (Phosgene), $\text{COCl}_2$ .

Carbonyl chloride is used in the preparation of Michler's ketone, crystal violet, a few azo dyes, etc., and is usually prepared in the colour works. It is also brought on the market in bombs or (in smaller quantities) dissolved in toluene.

It is prepared by passing an equal molecular mixture of chlorine and carbon monoxide over animal charcoal.

Carbonyl chloride is a malodorous liquid, which has a sp. gr. of 1.432 at  $0^\circ$ , and boils at  $8^\circ.2$ . It is very easily soluble in benzene or glacial acetic acid, and is decomposed slowly by cold water, rapidly by hot, yielding carbon dioxide and hydrochloric acid. It should not contain free chlorine; accordingly on treatment with potassium iodide at most a faint yellow colour should be formed but no brown, flocculent precipitate (iodine) should result.

### 13. Iodine.

Iodine is put on the market chiefly in two forms. The ordinary crude iodine consists of grey lumps of crystalline texture, and has the appearance of graphite; the purer resublimed iodine consists of grey, glistening leaflets. Iodine is used in the colour industry for the production of blue-shade eosins.

Its complete volatility and also its solubility in alcohol and in a solution of potassium iodide are frequently regarded as criteria of its purity, but do not furnish, however, a sufficient guarantee, since crude iodine very often contains iodine chloride, cyanogen iodide, and other volatile substances. With most kinds of iodine recourse must be had to quantitative estimation by titration with sodium thiosulphate or sodium arsenite.

The titre is obtained in the usual way by means of pure iodine or arsenious acid. In its examination about 10 g. of the finely-powdered average sample and twice the quantity of pure potassium iodide are dissolved and made up to a litre, and about 50 c.c. of the solution are taken for the analysis. Sodium thiosulphate or sodium arsenite is added in excess, and the excess of the reagent is titrated with  $N/10$  iodine until a faint blue coloration is produced in the starch-paste indicator.<sup>1</sup>

### 14. Bromine.

Bromine is a dark, reddish brown liquid which boils at  $63^\circ$  and volatilises even at the ordinary temperature. It solidifies in the

<sup>1</sup> Cf. Vol. I., pp. 112 *et seq.*

cold to \* glistening, metallic-looking leaflets which melt at  $7^{\circ}3$ . Its sp. gr. is 2.97 at  $0^{\circ}$ . It is sparingly soluble in water, easily so in glacial acetic acid or ether. Commercial bromine is usually almost pure, and can be used without further examination. It is employed in the colour industry for the preparation of ethyl bromide and for the production of brominated fluoresceins (eosin, etc.). Practically all bromine is obtained from the salts in the Stassfurt mother liquors by distilling these with manganese dioxide and sulphuric acid.

### 15. Hydrogen Peroxide, $H_2O_2$ .

The commercial product is usually a 3 per cent. solution of hydrogen peroxide, which often contains phosphoric acid and mineral salts such as sodium chloride, magnesium chloride, and sodium sulphate.

The percentage of hydrogen peroxide is estimated by titration with potassium permanganate.

One c.c. of the hydrogen peroxide solution is diluted to 300 c.c. with distilled water; about 30 c.c. of dilute sulphuric acid are added, and the mixture is stirred continuously while  $N/10$  potassium permanganate is added, drop by drop, until a faint permanent pink colour is produced.

One c.c. of  $N/10$  potassium permanganate contains 0.00316 g. of the crystallised salt, and represents 0.0017 g. of hydrogen peroxide.

The content of commercial hydrogen peroxide is frequently given as a volume percentage. This expression is intended to designate the quantity of oxygen gas produced by the decomposition of 1 c.c. of the hydrogen peroxide solution. One c.c. of 3 per cent. hydrogen peroxide solution evolves ten volumes of oxygen; such a solution is termed a 10-volume-per-cent. solution.<sup>1</sup>

### 16. Zinc Dust.<sup>2</sup>

Zinc dust is a by-product in the metallurgical production of zinc, and is a mixture which contains, in addition to metallic zinc, variable quantities of zinc oxide and small amounts of lead, cadmium, arsenic, etc. It is extensively employed in the colour industry as a very energetic reducing agent.

<sup>1</sup> Cf. also P. Sisley, on "The Analysis of Commercial Hydrogen Peroxide," *Rev. Gen. Mat. Col.*, 1901, 5, 209; 1904, 8, 167; also W. B. Dehn, *J. Amer. Chem. Soc.*, 1907, 29, 1315. For the estimation of acids in hydrogen peroxide, cf. Endemann, *Z. angew. Chem.*, 1909 22, 673. *J. Chem. Soc.*, 1909, 96, ii., 432; Lüning, *Z. angew. Chem.*, 1909, 22, 1549. *J. Chem. Soc.*, 1909, 96, ii., 826. For the valuation of sodium peroxide, cf. E. Rupp, *Arch. Pharm.*, 1902, 240, 437; *Chem. Zeit.*, 1905, 29, 443; H. Grossmann, *Chem. Zeit.*, 1905, 29, 137.

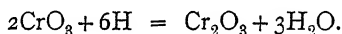
<sup>2</sup> Cf. this Vol., p. 295; also L. de Koninck and M. Grandry, *Bull. Assoc. Belge. des Chim.*, 1902, 16, 234; *J. Chem. Soc.*, 1903, 84, ii., 105. L. de Koninck, "Apparatus for the Gasometric Estimation of the Metal in Zinc Dust," etc., *Bull. Assoc. Belge. des Chim.*, 1903, 17, 112; *J. Chem. Soc.* 1903, 84, ii., 758; Wohl, *Ber.*, 1904, 37, 451.

Since the metallic zinc is the only effective constituent, its estimation is absolutely necessary in testing the quality. This can be done in different ways.

1. R. Fresenius proposes to estimate the percentage of zinc from the volume of hydrogen liberated by acids. Beilstein and Jawein have developed the method. A more suitable apparatus is described by F. Meyer.<sup>1</sup> The 'azotometer' (Vol. I., p. 125), the nitrometer with the attached bottle (Vol. I., p. 132), or the gas volumeter (Vol. I., p. 138), can also be employed for the purpose. A simpler apparatus has been described by O. Bach.<sup>2</sup>

In all these cases the volume of the evolved hydrogen is first obtained and reduced to the volume of dry gas at 0° and 760 mm. in the usual way. Since 1 litre of hydrogen weighs 0.08995 g., and the atomic weight of zinc is 65.4, the number of c.c. of hydrogen must be multiplied by 0.002919 in order to calculate the weight of available zinc in grams.

2. A more convenient method is that proposed by Drewsen,<sup>3</sup> which is based on the fact that finely divided metallic zinc reduces a solution of chromic acid (potassium bichromate and sulphuric acid) without the evolution of hydrogen, according to the equation :



The method is described on p. 298.

It must be noted that this, like all other methods depending on an estimation of the reducing power of zinc dust, does not determine the actual amount of metallic zinc.

Any cadmium and iron present likewise reduce the chromic acid, and are therefore always estimated as zinc, but this is immaterial since the commercial value of zinc dust is represented by its reducing power alone.

3. Perhaps the best method is that described by Wahl,<sup>4</sup> which is as follows:—0.5 g. of the zinc dust is shaken with 25 c.c. of cold water, and 7 g. of pure neutral ferric sulphate is added. In fifteen minutes the zinc will have dissolved (with the exception of impurities) with reduction of an equivalent quantity of the ferric salt, and without evolution of hydrogen if acid is absent. The solution is then acidified and titrated with permanganate. The ferric sulphate is prepared by oxidising a mixture of five parts of ferrous sulphate and one of sulphuric acid with excess of nitric acid, evaporating to dryness, grinding, and washing with alcohol until no longer acid, and drying thoroughly. A blank test is desirable.

<sup>1</sup> *Z. angew. Chem.*, 1894, 7, 131, 435.

<sup>2</sup> *Ibid.*, 1894, 7, 291.

<sup>3</sup> *Z. anal. Chem.*, 1880, 19, 50.

<sup>4</sup> *J. Soc. Chem. Ind.*, 1897, 16, 15.

G. Klēmp<sup>1</sup> recommends the estimation of zinc dust by boiling with a standard alkaline solution of potassium iodate.

By estimating the iodine liberated on acidification, the amount of the reduced iodate, and therefore that of the active zinc, is calculated. The method is not very practical, since the liberated iodine must be removed by distillation before being titrated.

### 17. Zinc Chloride, $\text{ZnCl}_2$ .

Anhydrous zinc chloride forms hard, fused sticks, or a dry, powdery mass. It rapidly absorbs moisture from the air, being transformed into a very caustic, viscous liquid. A large amount of heat is developed when it is covered with water, and it dissolves even in about 0.3 parts, forming a syrup. In the colour industry solid zinc chloride is used as a dehydrating agent; for example, in the preparation of tetramethyldiaminobenzophenone and crystal violet. Frequently it contains more or less zinc oxychloride, which is produced by the partial decomposition of the zinc chloride during the evaporation of its solution. The presence of the oxychloride is detected by the deposit of zinc oxide obtained when the zinc chloride is dissolved in water. The product should be tested for this impurity, the presence of which is, for many purposes, troublesome. In general, the zinc chloride may be regarded as satisfactory when one part gives a clear solution in ten parts of water. For its estimation 10 g. of the product under examination are dissolved in 100 c.c. of water and  $N/1$  acid is run in, with stirring, until the turbid liquid becomes clear. To detect the end-point more sharply, methyl orange can be used as indicator. One c.c. of  $N/1$  acid represents 0.10885 g. of zinc oxychloride, or 0.0407 g. of zinc oxide.

A persistent turbidity or perhaps a heavy precipitate, which dissolves on warming, indicates the presence of lead.

In addition to this, its reaction is examined, the amount of water is determined by ignition in a porcelain crucible, and qualitative tests are made for sulphuric acid, nitric acid, iron, and lead. Hydrogen sulphide is passed into an ammoniacal solution until the metals are completely precipitated, and the filtrate is evaporated. Any residue left after ignition is examined for sodium chloride, calcium chloride, magnesium chloride, and similar impurities.

Zinc chloride is frequently used in solution, and is employed in this condition chiefly for the isolation of certain dyes; for example, methylene blue, in the form of the zinc double salts.

The solution of zinc chloride necessary for this purpose is usually prepared directly by dissolving scrap zinc in hydrochloric acid.

A table of the specific gravity of solutions of zinc chloride is given on p. 367.

<sup>1</sup> *Z. anal. Chem.*, 1890, 29, 253.



### 18. Ferric Chloride.

Only hydrated ferric chloride,  $\text{Fe}_2\text{Cl}_6 \cdot 6\text{H}_2\text{O}$ , is employed technically. It consists of yellowish brown crusts, which deliquesce in moist air and should give a moderately clear solution in water. The solution has a yellowish brown colour, an acid reaction, and an astringent taste.

The presence of ferrous chloride as an impurity is detected by the blue colour developed by treating a solution of the product with potassium ferricyanide. The presence of nitric acid is detected by the usual methods.

Ferric chloride is employed in the colour industry as an oxidising agent; for example, in the production of Helvetia blue, for the preparation of a brand of malachite green (probably the iron double salt), and for the decomposition of the copper compound of methyl violet, etc.

A qualitative examination of ferric chloride is usually sufficient, since it is a cheap material and no great demands as to its purity are required. The composition of its solutions is determined, with sufficient accuracy, by the specific gravity. Franz's table (p. 362) suffices for the calculation.

When an accurate estimation is required, the iron which is present as ferrous chloride is first determined by titration with potassium permanganate; in a second experiment, the total iron is determined similarly, after reducing the ferric chloride with zinc and sulphuric acid. The difference represents the iron present as ferric chloride.

### 19. Lead Peroxide,<sup>1</sup> $\text{PbO}_2$ .

The commercial product is a dark brown powder or a brown paste, and can be prepared, for example, by treating a solution of lead acetate with a solution of calcium hypochlorite.

According to the conditions under which it is prepared, the product is a more or less compact mass, the efficiency of which, as an oxidising agent, varies very greatly with its physical condition. Experience alone must decide what quality is most suitable for any particular purpose.

The examination for impurities is conducted as follows:—A few grams are boiled with ten to twelve times the quantity of water and a little dilute nitric acid, and the solution is filtered. A portion of the filtrate should not produce a turbidity with silver nitrate (absence of chlorides); another portion should not leave a residue after evaporation. If obtained, the residue is examined for calcium and lead.

<sup>1</sup> Cf. also p. 533.

Sulphuric acid is detected by warming a sample with a concentrated solution of sodium hydrogen carbonate, filtering, and treating the filtrate with an excess of hydrochloric acid and barium chloride. Another sample is dissolved in concentrated sulphuric acid, and the mass, after cooling, is treated with water and a fresh quantity of the substance under examination. The formation of a red colour in the solution indicates the presence of manganese.

To estimate its value, 3 to 4 g. of the powder or about 10 g. of the paste are weighed, and decomposed by shaking for one hour in a litre flask with 100 c.c. of  $N/2$  oxalic acid, 150 c.c. of dilute sulphuric acid (1:3), and distilled water (for rinsing). The contents of the flask are made up to a litre and filtered; 250 c.c. of the filtrate are treated with 50 c.c. of dilute sulphuric acid and a little distilled water, and the excess of oxalic acid present is titrated with  $N/5$  potassium permanganate. Lead peroxide is employed for the oxidation of leuco bases (tetramethyldiaminotriphenylmethane), etc.

## 20. Stannous Chloride (Tin Salt).

Hydrated stannous chloride,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , which is alone employed technically, forms transparent crystals which are very easily soluble in water and deliquesce in moist air. Stannous chloride oxidises moderately rapidly in the air, yielding partly stannic chloride, partly an oxychloride. On solution in water, the latter leaves a considerable residue of tin oxide. Pure stannous chloride gives a clear solution in air-free water, but such a degree of purity cannot be expected of the technical product.

A common adulterant of tin salt is magnesium sulphate, which differs only slightly from it in appearance. It must be tested, therefore, with barium chloride, for any noticeable amount of sulphate. When a small quantity of its solution is precipitated by hydrogen sulphide and the filtrate is evaporated, only an inconsiderable residue should be obtained.

The actual amount of stannous chloride is best ascertained by titrating, with  $N/10$  iodine, a solution which contains tartaric acid and is made strongly alkaline with sodium hydrogen carbonate.

Its quality is best ascertained by an estimation of the tin, the clearness of the aqueous solution being also taken into consideration.

A. Fränkel<sup>1</sup> treats its solution in hydrochloric acid with an excess of potassium bichromate, then adds potassium iodide, and titrates the liberated iodine with sodium thiosulphate.

A table of the specific gravity of stannous chloride solutions is given on p. 372.

<sup>1</sup> *Mitt. techn.-Gew. Museums*, 1892, 223.

## 21. Stannic Chloride.

Hydrated stannic chloride,  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , forms a deliquescent mass and is very easily soluble in water. In dyeing, it is chiefly used as an extremely important mordant and weighting material. It should be free from stannous chloride, and therefore should not produce a turbidity in a solution of mercuric chloride.

An estimation of the tin is the best means of ascertaining the quality. Since, however, it is generally employed in solution, the determination of the specific gravity, from which the composition can be ascertained by means of tables (*cf.* p. 373), is usually regarded as satisfactory for this purpose.

O. Geisel<sup>1</sup> proposes a new, technical method for the estimation of tin, especially that in "pink" baths.

In such dilute solutions of stannic chloride, the hydrochloric acid is estimated by titration with  $N/10$  alkali, whilst the tin is estimated gravimetrically as the dioxide,  $\text{SnO}_2$ . The titration is often carried out by precipitating all the tin (an excess of precipitant must be avoided), filtering, and titrating the filtrate again, using phenolphthalein as indicator. For example, when analysis of "pink" baths for weighting silk are required, equal quantities of the liquid are diluted to the same extent. If the proportions of tin and acid in the bath do not alter materially, and if the bath is always made up to the same sp. gr., the same number of c.c. of  $N/10$  alkali are nearly always required to precipitate the tin. It is then sufficient to test once when all the tin is precipitated. An excess of a few tenths of a c.c. do not appreciably affect the result, but larger quantities would cause a considerable error.

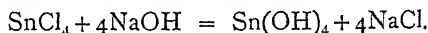
A simpler and yet sufficiently accurate method is direct titration (without filtering), using methyl orange as indicator.

The old method of estimating tin (precipitation of the boiling dilute solution by ammonium nitrate, filtration, washing, burning of the wet filter, ignition, and weighing) is rather tedious. Geisel recommends a method based on the following observation. In a solution of stannic chloride, containing 0.075 to 0.100 g. of stannic oxide in 10 c.c., the whole of the tin is precipitated quantitatively in the cold by sodium hydroxide before the hydrochloric acid is completely neutralised. With various dyes stannic chloride forms lakes of a different colour, and malachite green is suitable as an indicator for this purpose. When a few drops of a 1 per cent. solution are added to a solution of stannic chloride of the above-mentioned concentration, a golden yellow colour with a green shade is developed. The solution is titrated with  $N/10$  sodium

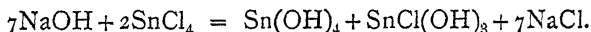
<sup>1</sup> *Chem. Zeit.*, 1902, 26, 553.

hydroxide. Since the change to the original bluish green colour of the malachite green solution is not very sharp, the operation is performed in a large beaker, which is placed on a white tile; the colour produced in its immediate neighbourhood by the introduction of a drop of the alkali is compared with the colour of the surrounding liquid, the mixture is then shaken, and the titration is continued until the last drop of alkali does not produce a colour bluer than that of the surrounding liquid.

With a little care, very concordant results are obtained. If the amount of stannic oxide is calculated from the volume of sodium hydroxide used, according to the equation:—



The results obtained are lower than the true values, determined gravimetrically; both, however, are in a constant ratio, which is expressed by the following equation:—



Calculated by means of this equation, the amounts of  $\text{SnO}_2$  agree fairly well with those obtained by the gravimetric method.

The volumetric method with malachite green as indicator is inaccurate in the presence of an excess of hydrochloric acid.

## 22. Arsenic Acid.

Arsenic acid is employed in the colour industry in the form of a viscous, aqueous solution, which has a sp. gr. of 1.85 to 2.0. The proportion of arsenic oxide varies between 60 and 70 per cent. An acid containing about 63 per cent. is most frequently used; it has a sp. gr. of 1.95 (approx.). Arsenic acid finds scarcely any application other than in the production of magenta. For this purpose its quality is of great importance. Above all, it must be free from nitric acid, which can be easily detected by the usual tests. Moreover, it ought not to contain, at the most, more than 0.5 to 1 per cent. of arsenious acid. The latter is readily estimated by neutralising the acid with sodium hydrogen carbonate and titrating with *N*/10 iodine; the acid should also remain fairly clear when made strongly alkaline with ammonium hydroxide. An appreciable precipitate indicates the presence of calcium, which frequently occurs in commercial arsenic acid as the hydrogen arsenate.

It is generally sufficient always to use arsenic acid of the same specific gravity, the approximate purity of which has been ascertained by qualitative examination. Up to the present, a serviceable table has not been compiled for calculating the content of arsenic acid from the specific gravity. H. Schiff's table relates only to specific gravity from 1 to 1.7, and is useless, therefore, for the present purpose.

The following table, compiled by R. Nietzki, should be of use, even though it does not pretend to great accuracy in all particulars :—

Spec. Grav. at 16°	Percentage of $As_2O_5$	Spec. Grav. at 16°	Percentage of $As_2O_5$
1.761	56.5	2.003	66.5
1.781	57.4	2.071	67.7
1.803	58.3	2.112	68.9
1.826	59.2	2.157	70.2
1.850	60.1	2.205	71.7
1.875	61.1	2.257	72.9
1.903	62.1	2.314	74.3
1.932	63.5	2.364	75.5
1.964	64.2	2.446	77.4
1.997	65.3		

Since it frequently happens that the specific gravity of arsenic acid is increased by the addition of sodium arsenate, it is particularly important to prove its almost complete volatility. A convenient method is to treat the acid with a little pure sugar and ignite to a full red heat. Pure arsenic acid ought to leave only an inconsiderable residue.

### 23. Fuming Sulphuric Acid.

A detailed account of the properties and methods of analysis is given in Vol. I., pp. 387 *et seq.*

### 24. Phosphoryl Chloride, $POCl_3$ .

Phosphoryl chloride is prepared by distilling one part of anhydrous oxalic acid with two parts of phosphorus pentachloride, or by treating phosphorus trichloride with potassium chlorate.

It is a colourless, refractive liquid, which boils at  $110^\circ$  and has a sp. gr. of 1.7.

Its purity is ascertained by a determination of the specific gravity and by fractional distillation.

Phosphoryl chloride is employed in the preparation of Victoria blue, night blue, and other dyes.

### 25. Ammonium Hydroxide.

Solutions of ammonium hydroxide of very different concentration and purity are employed in the colour industry. The crude liquid, obtained as a by-product in the manufacture of coal gas, is largely contaminated with empyreumatic substances, which are detected, after neutralisation with acid, by their odour. For most purposes ammonium hydroxide must be rejected if it contains sulphur. The presence of sulphur is easily shown by a solution of a lead salt. In most cases the

specific gravity suffices for the estimation of ammonium hydroxide. When greater accuracy is demanded, recourse must be made to titration. The analysis of ammonium hydroxide and of ammonium salts is described in detail on pp. 740 *et seq.*

## 26. Sodium Nitrite, $\text{NaNO}_2$ .

The actual  $\text{NaNO}_2$  is alone of importance in judging the quality of sodium nitrite; the sodium nitrate, which is always present, is valueless for the purposes of the colour works. For this reason, methods which are based on the determination of the total nitrogen (by the nitrometer or in other ways) are inapplicable for its estimation. The only practical methods are the potassium permanganate and the sulphanilic acid processes.

Lunge<sup>1</sup> has compared the various modifications of these processes, and arrives at the following conclusions:—Feldhaus' original method, in which potassium permanganate is run into an acidified solution of sodium nitrite until a persistent red colour is produced, leads inevitably to a loss owing to the decomposition of nitrous acid into nitric oxide and nitric acid, whereby a portion of the nitric oxide escapes, as is proved by its odour. Consequently the results are very variable and considerably too low. On the other hand, accurate results are obtained when the method described by Lunge<sup>2</sup> in 1877 is used, in which the solution of nitrous acid, in this case an aqueous solution of sodium nitrite, is run into a known volume of potassium permanganate which has been strongly acidified with dilute sulphuric acid and warmed to  $40^\circ$ – $50^\circ$ ; the nitrite is introduced slowly and the mixture must be well shaken. The end of the reaction is reached as soon as the pink colour has just disappeared. For example, 20 c.c. of  $N/2$  potassium permanganate (or 100 c.c. of  $N/10$ ) are acidified with sulphuric acid, warmed as above, and treated with a solution of 1 g. of sodium nitrite in 160 c.c. of water from a burette until decolorisation is just effected: 1 c.c. of  $N/2$  potassium permanganate represents  $\frac{69.01 \times 0.004}{16}$

—that is, 0.01725 g. of actual sodium nitrite; therefore 20 c.c. correspond with 0.3450 g. of sodium nitrite, or 34.50 c.c. of a 1 per cent. solution of chemically pure sodium nitrite. If  $n$  c.c. of the nitrite solution are actually used, the percentage of  $\text{NaNO}_2$  in the nitrite is  $\frac{3450}{n}$ . The method is accurate to 0.1 per cent. Kinnicutt's method<sup>3</sup> is equally accurate.  $N/10$  potassium permanganate is run slowly into a neutral solution of sodium nitrite until a persistent red colour is produced, a

<sup>1</sup> *Z. angew. Chem.*, 1891, 4, 629.

<sup>2</sup> Vol. I., p. 343.

<sup>3</sup> *Proc. Amer. Acad.*, 1883, 275; *Chem. News*, 1883, 48, 274.

few drops of sulphuric acid are then added, followed by an excess of the potassium permanganate, the mixture is strongly acidified and heated to boiling, and the excess of the potassium permanganate is titrated with *N*/10 oxalic acid. The method is more elaborate, but not more accurate, than Lunge's.

A method employed very commonly in colour works is diazotisation on the small scale; a solution of sodium nitrite is run into aniline cooled with ice, until potassium iodide-starch paper is turned blue.

The use of sodium sulphanilate is recommended by various chemists.<sup>1</sup>

In this process 14.4375 g. of sodium sulphanilate are dissolved in 250 c.c.; 1 c.c. of this solution represents 0.01727 g. of nitrite.

Fifty c.c. of the sulphanilate solution are diluted to 250 c.c. and treated with 10 c.c. of hydrochloric acid. A solution of the nitrite (about 23 g. in a litre of water) is run in until potassium iodide-starch paper is turned blue. The end-point is reached when the colour is produced instantly and persists for a few minutes.

The results obtained by this method agree satisfactorily with those of the permanganate process, provided that absolutely pure sodium sulphanilate, dried over sulphuric acid, and freshly prepared starch solution<sup>2</sup> are employed.<sup>3</sup> A suitably pure salt is obtained by repeatedly crystallising sodium sulphanilate, drying it well between filter-paper, and allowing it to remain for two days in a desiccator over concentrated sulphuric acid.

*p*-Toluidine can be used instead of sodium sulphanilate, if the experiment is performed in strongly acid solution.<sup>4</sup>

Technical sodium nitrite contains usually 97 to 98 per cent. of actual sodium nitrite.

## 27. Potassium Bichromate, $K_2Cr_2O_7$ .

Potassium bichromate is an extremely important oxidising agent and is employed in the manufacture of alizarin for the conversion of anthracene into anthraquinone. The methods of analysis, etc., are given on p. 323.

## 28. Sodium Bichromate, $NaCr_2O_7$ or $Na_2Cr_2O_7, 2H_2O$ .

Potassium bichromate is being displaced more and more by the cheaper and much more easily soluble sodium bichromate. This forms small, readily soluble, reddish yellow crystals, which soon become moist in the air (*cf.* this Vol., p. 365). An estimation of the chromic acid by the methods described (*loc. cit.*), should always be performed,

<sup>1</sup> Schultz, Vaubel, *Z. Farb. Ind.*, 1902, 1, 37, 149, 339.

<sup>2</sup> Lunge, *Chem. Zeit.*, 1904, 28, 501.

<sup>3</sup> *Cf.* also Wegner, *Z. anal. Chem.*, 1903, 42, 159.

<sup>4</sup> Vaubel, *Die phys. u. chem. Methoden d. quant. Bestimmung Org. Verb.*, 1902, II., 251.

since the purity of this salt can be less readily guaranteed than that of potassium bichromate.

### 29. Sodium Sulphide.

The commercial product,  $\text{Na}_2\text{S}$ ,  $9\text{H}_2\text{O}$ , has a yellow or dark brown colour. The usual impurities are free alkali and sodium thiosulphate.

M. Battagay's volumetric process<sup>1</sup> depends on the fact that zinc thiosulphate is soluble in water, and consequently can be converted into zinc sulphide by sodium sulphide.

A solution of the sodium sulphide, under examination is treated with acetic acid until the indicator, phenolphthalein, changes from red to colourless, so that the zinc salt can no longer be attacked by the alkali. A standard solution of zinc sulphate,  $\text{ZnSO}_4$ ,  $7\text{H}_2\text{O}$ , is then run in until all the sodium sulphide has been converted into insoluble zinc sulphide.

To detect this point, a coloured indicator is required which will show the presence of the soluble sulphide and yet not be affected by zinc sulphide in the cold. Cadmium sulphate satisfies these conditions. Thick, white blotting-paper (not ordinary filter-paper) is "spotted" with a concentrated solution of cadmium sulphate, and drops of the titrated liquid are placed on the marks. Yellow cadmium sulphide is formed so long as alkali sulphide is present. The end-point can be recognised very sharply after a little practice (*cf.* Vol. I., p. 425).

Another volumetric method is due to Podreschetnikoff.<sup>2</sup> 9.052 g. of the sample are dissolved in 500 c.c. of air-free distilled water; 10 c.c. of this solution are diluted with 150 c.c. of water and titrated with  $N/10$  sulphuric acid, using phenolphthalein as indicator (requiring, say, 12.8 c.c.). An excess (about 10 c.c.) of neutral formaldehyde solution is now added, and  $N/10$  acid run in until the solution again becomes colourless, the amount of acid required being, say, 12.5 c.c. The calculation (using the above amounts of acid as example) is then as follows:—

In 100 c.c. the free  $\text{NaOH} = 12.8 - 12.5 \text{ c.c.} = 0.3 \text{ c.c.}$

$N/10$  solution  $= 0.0012 \text{ g.} = 0.66 \text{ per cent.}$

$\text{NaOH}$  from  $\text{Na}_2\text{S} = 12.5 \text{ c.c. } N/10 \text{ solution} = 0.05 \text{ g.}$   
 $\text{NaOH}$  „  $\text{NaSH} = 12.5 \text{ c.c. } N/10 \text{ solution} = 0.05 \text{ g.}$  }  $= 53.85 \text{ per cent. } \text{Na}_2\text{S}.$

Sodium sulphide is employed in large quantities in the preparation of sulphur dyes, and in their application in dyeing.

### 30. Water-Glass.

Water-glass is prepared by fusing sand with sodium carbonate or potassium carbonate, or a mixture of the two, with an alkali sulphate

<sup>1</sup> *Z. Farb. Ind.*, 1903, 2, 349.

<sup>2</sup> *Ibid.*, 1907, 6, 388.



or alkali chloride in the presence of wood-charcoal, or by dissolving flint, which has been ignited and disintegrated by water, or kieselguhr in alkali hydroxide under pressure. The solid commercial product is a whitish, glassy mass; through the presence of iron it is frequently coloured greenish (ferrous oxide) or greyish yellow (ferric oxide).

It is frequently brought on the market as a double silicate in the form of an aqueous solution (sp. gr. 1.26 to 1.30) containing more than 70 per cent. of silica. The solutions must be excluded from air to prevent the separation of gelatinous silicic acid.

Its applications are various: it is added to soap and to varnishes; it is used for rendering materials fireproof, for the preparation of artificial stone and cement; it is employed in stereochrome work, in finishing and dyeing, and especially in conjunction with stannic chloride and sodium phosphate for weighting silk, in bleaching with hydrogen peroxide, etc.

Good water-glass should dissolve completely in warm water, or leave only a very slight residue. In its examination attention must be paid to the amounts of silicic acid, combined alkali, and neutral salts (such as sodium chloride); alkali sulphide and compounds of lead and iron may also be present. The composition of solutions of water-glass can be estimated by a determination of the specific gravity.

The silicic acid is estimated by the usual methods, or volumetrically by conversion into potassium silicofluoride,<sup>1</sup> or by direct titration with  $N/1$  acid, using methyl orange as indicator.

P. Heermann<sup>2</sup> recommends the following method for the estimation of the free alkali and of the chief constituents:—

*Estimation of the Free Alkali.*—The only method depends on the precipitation of the unchanged water-glass with alcohol and sodium chloride, and titration of the filtrate.

Sodium chloride alone does not precipitate the water-glass completely; alcohol alone causes a quantitative precipitation, but the resulting pasty mass is almost unfilterable. By using both reagents, good results are obtained.

Ten grams of water-glass are treated with 100 c.c. of a neutral saturated solution of sodium chloride, and the pasty mass is then diluted to 200 c.c. with neutralised alcohol; 100 c.c. of the filtrate are titrated with  $N/10$  acid, using phenolphthalein as indicator.

An alternative process is to treat 10 g. of water-glass and 100 c.c. of water with 20 c.c. of saturated sodium chloride, dilute with neutralised alcohol to 250 c.c., and titrate the filtrate as above.

(According to this example, the amount of sodium chloride may vary, apparently, between considerably wide limits.)

<sup>1</sup> Stolba, *Z. anal. Chem.*, 1865, 4, 163.

<sup>2</sup> *Chem. Zeit.*, 1904, 28, 879, 883.

In another process, barium silicate is precipitated by a large excess of barium chloride in the cold.

Ten grams of water-glass are diluted with about 100 c.c. of cold distilled water. To this solution a cold solution of at least 10 g. of barium chloride in about 100 c.c. of water (for example, 100 c.c. of  $N/1$  barium chloride) is added in a fine stream with continuous shaking. The mixture is diluted to 250 c.c., thoroughly shaken, and passed at once through a dry filter. Rejecting the first 20 to 30 c.c., 100 c.c. of the filtrate are titrated with  $N/10$  hydrochloric or sulphuric acid, using phenolphthalein as indicator. The number of c.c. of  $N/10$  acid used, multiplied by 0.0775, gives the percentage of free alkali as  $\text{Na}_2\text{O}$ , or multiplied by 0.1, the percentage of free alkali as sodium hydroxide,  $\text{NaOH}$ . Only the alkali present as the hydroxide is thus estimated, since any sodium carbonate in the silicate is precipitated as barium carbonate. In estimating the chief constituents, about 15 to 20 g. of water-glass are dissolved in distilled water and diluted to 500 c.c. The solution should be absolutely clear, and should not give a deposit after keeping for several days.

*Free and Combined Alkali.*—One hundred c.c. of the preceding solution are titrated with  $N/1$  or  $N/2$  hydrochloric or sulphuric acid, using methyl orange as indicator; 1 c.c. of  $N/1$  acid represents 0.031 g. of  $\text{Na}_2\text{O}$  or 0.04 g. of  $\text{NaOH}$ .

*Silicic Acid.*—Another 100 c.c. of the solution are treated with concentrated hydrochloric acid in a platinum basin, evaporated to dryness on the water-bath, repeatedly moistened with hydrochloric acid and evaporated, the residue dried in an air-oven at  $120^\circ$  for one and a half to two hours, extracted with warm dilute hydrochloric acid, filtered, washed thoroughly, dried, ignited strongly, and weighed as silica.

As a test of its purity, the silica can be converted into volatile hydrofluosilicic acid by treatment with hydrofluoric and sulphuric acids. Any residue left after a repetition of the treatment is not silica, and its weight must be subtracted from that found.

*Sodium Chloride, Neutral Salts.*—The filtrate from the silicic acid is treated with ammonium hydroxide, ammonium carbonate, and ammonium oxalate, warmed for a short time on the water-bath, kept for twenty-four hours, and filtered. The filtrate is evaporated, and the residue, after the removal of the ammonium salts by gentle ignition, is heated until its weight is constant; it consists of sodium chloride, etc. The amount, calculated as  $\text{Na}_2\text{O}$ , is added to that of the free and combined alkali, thus giving the total amount of alkali.

*The Combined Alkali* is determined by subtracting the amount of free alkali from that of the free and combined alkali.

In criticising this process, Jordis<sup>1</sup> states that it contains many

<sup>1</sup> *Chem. Zeit.*, 1905, 29, 33.

points which require explanation, and that concordant results can only be expected when all the conditions are strictly defined and are observed by all investigators. The analysis can only determine the proportions and the quantities of the chief constituents and the impurities in the solution, but furnishes no evidence for the statement that so much "free alkali" and so much "water-glass" is present. The term "water-glass" in itself designates, not a single chemical substance, but a very variable mixture of silicates. Moreover, one and the same water-glass contains, according to its temperature and state of dilution, different quantities of "free alkali," because the degree of hydrolysis, which determines the amount of free alkali, is dependent on these two factors. The "precipitation of the water-glass" is due to the fact that the silicate is to some extent "salted out" by the alcohol and sodium chloride, leaving a portion in the solution. This soluble portion, however, does not consist of alkali alone, but contains a small quantity of silicic acid; it is this portion, not the free alkali, which is estimated by the titration. Even though all the silicic acid were precipitated and actually only the free alkali remained in the solution, it would still not be permissible to assert that the latter is estimated by the titration, for its amount would be much less than the amount of "free alkali" in the original solution of water-glass, because by the addition of the sodium chloride and the alcohol, the extent of the hydrolysis, and therewith the concentrations of the sodium and the hydroxyl ions, would be largely diminished. Moreover, in addition to this, every solution of water-glass contains sodium carbonate, which would not be precipitated.

The precipitation as barium silicate by means of barium chloride is in no way quantitative, for the precipitated silicate always carries down a comparatively large quantity of alkali.<sup>1</sup>

Phenolphthalein is quite unsuitable as an indicator in the titration of water-glass, because solutions of all commercial water-glass contain carbonate, the amount of which increases with the age of the solution. The carbonate is not indicated by phenolphthalein. There is, however, no objection to the use of methyl orange.

## PART II

### DYES

#### General Remarks.

In the laboratory the method of examination of finished dyes may be of two kinds:—

1. A dye, the nature and derivation of which is unknown, requires a determination of its chemical composition and constitution, and its method of preparation should also be ascertained.

<sup>1</sup> Jordis and Kanter, *Z. anorg. Chem.*, 1903, 35, 82, 148, 336; 1904, 42, 418.

2. A known product should be examined as to its dyeing value, *i.e.*, its shade, dyeing power, purity, and genuineness.

In the former case, an attempt should also be made to ascertain the behaviour of the dye on the fibre or its dyeing properties, because by these means important evidence for the recognition of the substance may be gained; not until then is the way open for the detailed examination (see below).

Quantitative dye trials against a known standard, the so-called "type," are employed, almost without exception, as a control of the products of the colour-works and for the valuation of the commercial product. All other proposals suggested for this purpose—for example, titration with sodium thiosulphate or calcium hypochlorite, the application of colorimetric methods, etc.—are worthless in practice. The same is true of G. Ullmann's process<sup>1</sup> for testing basic dyes.

Only in rare cases are dyes brought on the market as pure chemical compounds. Usually they contain larger or smaller quantities of an indifferent diluent—for example, sodium chloride, sodium sulphate, dextrin, sugar, etc. The first may have been introduced during the process of manufacture; in larger or smaller amount it is met with in all products the precipitation of which has been effected by sodium chloride. Very often, however, it is purposely added to the product, and so also are the other above-mentioned substances. Such additions are by no means to be condemned as adulteration; it will be shown later that they are necessary for various reasons. In the process of manufacture, the strength and the purity of the isolated product are not always the same; sometimes it has a greater, at others a weaker, dyeing value. The consumer, however, requires an article of uniform quality throughout. He will certainly know how much of the dye he requires to produce a definite shade on a definite quantity of wool, silk, etc. The manufacturer, therefore, cannot do otherwise than take as the type the product of weakest dyeing value obtained in the manufacture, and dilute stronger products to the standard strength by the addition of an indifferent material. Dyes frequently undergo still further dilution when they reach the retailer, especially in the East.

Often only a few units per cent. of the dye are present in products which, on account of their application for some specific purpose, must be cheap and must not contain more than a certain amount of colouring matter.

In many instances, especially in the case of costly products of great dyeing value, the consumer demands a cheaper article, even though of smaller dyeing value, in order to reduce the expense of the waste which is unavoidably incurred by the workman in weighing, etc.

<sup>1</sup> *Chem. Zeit.*, 1899, 23, 1014; *cf.* also A. Heinemann, "Criticism of G. Ullmann's Process," *Chem. Zeit.*, 1900, 24, 58.

It is obviously necessary, in such circumstances, that both buyer and seller should be able to ascertain the percentage of dye in the product.

Before accurately quantitative dye-trials can be discussed in detail, it is necessary to know the conditions under which different dyes are fixed on the fibre. In general, coal tar dyes possess a tendency to unite directly with fibres of animal origin, such as wool and silk. Many dyes lack this property in the case of fibres of vegetable origin, such as cotton and flax. These must be fixed by means of suitable chemicals such as tannic acid, alumina, tin oxide, etc., which form with the dyes insoluble compounds, the so-called lakes. A few fibres of plant origin—for example, jute—have the property of fixing most dyes without the aid of such mordants. On the other hand, many dyes are known which dye unmordanted cotton. The circumstances in which dyes can be fixed on animal fibres are extremely varied. Thus most dyes consisting of salts of organic bases are only effective in neutral or faintly acetic acid baths. The addition of a mineral acid or of an acid salt prevents almost completely the deposition on the fibre. Magenta, a large number of its derivatives, and other dyes belong to this class of so-called "basic dyes." Conversely, the presence of a mineral acid or of an acid salt is necessary in the case of dyes which have an acid character. This class comprises the "acid dyes," and to it belong most of the sulphonic acid and phthalein dyes. A few sulphonic acids—for example, diphenylrosanilinesulphonic acid—possess the property of combining, in the form of their salts, with the fibre in faintly alkaline solution. The fibre is thus much more uniformly permeated. Finally, the dye is developed completely in an acid bath. Such dyes are termed "alkali dyes."

A fourth class includes those dyes which are never fixed alone on the fibre, but always in the form of their most characteristic metallic lakes. Alizarin and its analogues, galloxyaniline, cœrulein, galloflavin, and many other dyes belong to this class.

In estimating the value of a dye by dye-trials, the first step is to ascertain to which of the four preceding classes the dye belongs; then a dye of known strength and of as nearly as possible the same shade is selected as the type.

The following criteria are of service in this qualitative test, which is useful chiefly for purposes of classification:—

*Substantive Cotton Dyes.*—A strip of calico or a small skein of cotton is boiled for about ten to fifteen minutes in a solution of the dye containing a little soap or sodium carbonate or sodium phosphate, and is then rinsed. The cotton is distinctly dyed and the bath is more or less exhausted. If the solution is still strongly coloured, a second, and possibly a third, strip is treated in a similar manner.

*Basic Dyes.*—Intensely coloured precipitates are produced when a solution of a basic dye is treated with a solution of tannin and sodium acetate; in neutral baths, animal fibres are dyed in full shades, cotton only feebly.

Wool, silk, or tannin-mordanted cotton are circulated in the warm solution for about fifteen minutes; dyeing is effected if a basic dye is present.

*Acid Dyes.*—As a rule, cotton is not dyed, or only very slightly; and also wool, in a neutral bath, is not affected, but as soon as a little sulphuric acid is added to the warm solution, the wool is rapidly dyed and the bath is very quickly exhausted. These dyes are of no importance for cotton, but are very extensively employed in dyeing animal fibres.



*Mordant Dyes.*—If cotton and wool, in a neutral, acid, or alkaline bath, are not dyed, or only in poor shades, the dye is probably a mordant dye. If this is the case, mordanted wool or cotton is placed in the warm bath, manipulated for fifteen to thirty minutes, washed, and eventually dipped in a brightening (soap) bath.

In these trials it is advantageous to use strips of calico which have been impregnated with streaks of different mordants. By this means several lakes are obtained, side by side, in a single, rapidly completed dye-trial, and from their nature it is often possible immediately to deduce far-reaching conclusions as to the nature and composition of the dye.

### Dye-trials.

To achieve success in a dye-trial necessitates experience in the particular branch of dyeing which deals with the dye in question; a trustworthy judgment of the result as regards colour, strength, shade, purity, etc., is possible only by the trained eye.

The following apparatus is required for really quantitative dye-trials:—

1. A few graduated pipettes, measuring cylinders, and measuring flasks.
2. Suitable dyeing-vessels: Glass beakers (for example, conical hard-glass beakers of about 400 c.c. capacity<sup>1</sup>), porcelain beakers or basins; beakers or basins of tinned copper of 300 to 1000 c.c. capacity, which can be heated directly over the gas or in water, oil, steam, calcium chloride, or glycerol baths.
3. A suitable number of glass rods of  or  shape for suspending and withdrawing the skeins.

To secure uniform heating, it is convenient to place several dyeing vessels in a rectangular or circular tin or copper bath, thus forming a

<sup>1</sup> R. Lepetit, *Färber-Zeit.*, 1893-94, 5, 183.

dyeing battery. Contrivances of this kind have been described or constructed by Marshall,<sup>1</sup> Whiteley,<sup>2</sup> and Kapff.<sup>3</sup>

A simple and practical arrangement is shown in Fig. 140.

It consists of a rectangular copper case standing on four iron feet and designed for the simultaneous reception of six porcelain beakers

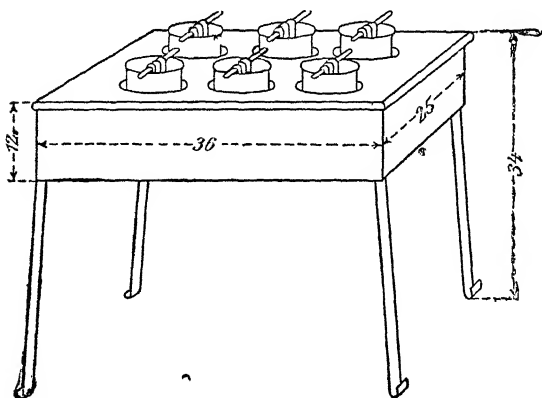


FIG. 140.

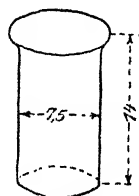


FIG. 141.

(Fig. 141). The latter do not rest directly on the bottom of the bath, but on a perforated copper plate situated several cm. above this. The case contains water, glycerol, etc., and is heated by gas or by steam; in the latter case a closed steam-coil is fitted between the perforated plate and the bottom of the bath.

When numerous simultaneous dye-trials are constantly being made, larger baths with eight to twelve apertures may be used; by arranging many such copper vessels in a suitable frame, all of the trials can be easily watched, and it is possible to work rapidly. Such an arrangement is shown in Figs. 142 and 143.

For experiments in which small variations of the temperature can affect the final result, it is well to select a bath of circular cross-section, and to fit between the bottom and the perforated plate a perforated disc, by the rotation of which uniform heating is attained.

The following general rules must be observed in performing comparative dye-trials.

1. The fibre used in the trial must be the same material to which the dye will be applied on the large scale. (Exceptions are permissible in many cases; basic dyes can often be tested on silk or wool in order to avoid the necessity of mordanting cotton with tannin.)

2. The dyeing, or the mordanting and all other operations must be performed under as nearly as possible the same conditions as those which prevail on the large scale. It is not, however, always

<sup>1</sup> *J. Soc. Chem. Ind.*, 1893, 12, 909, 996.

<sup>2</sup> *Ibid.*, 1891, 10, 521.

<sup>3</sup> *Färber-Zeit.*, 1898, 9, 357.



FIG. 142.

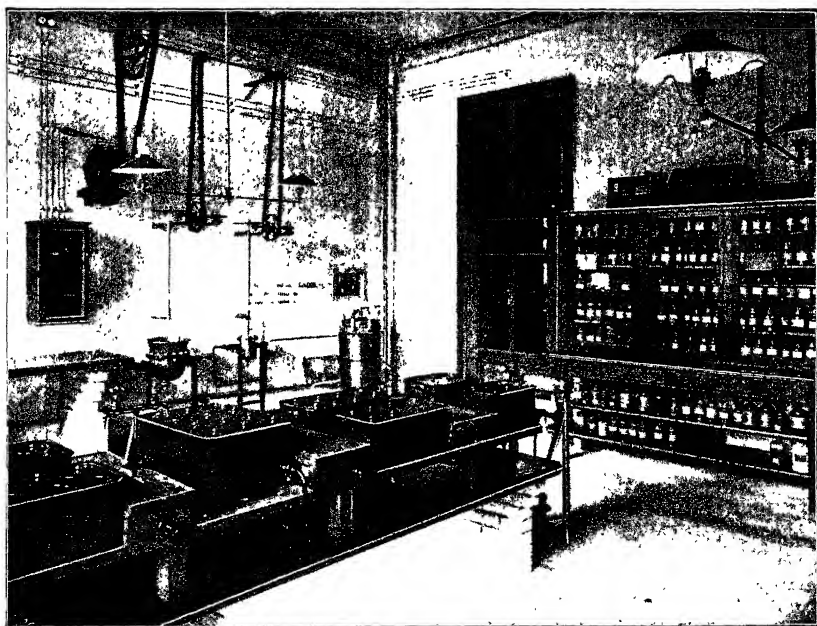


FIG. 143.





possible to reproduce the same conditions; in a laboratory experiment the warming is often more rapidly accomplished, the fibre comes more frequently into contact with the walls of the vessel. the conditions with regard to the access of air are different, etc. Moreover, it must be remembered that in dyeing on the large scale baths are in use often for long periods, adequate quantities of fresh dye-solution being added from time to time before the introduction of fresh batches of goods. This custom may lead to results different from those of the dye-trial, especially if a mixture of dyes, the individual constituents of which produce uneven dyeing, is being used.

3. As a rule, the dye under examination must be compared with a standard of known strength, the so-called type, the trials with the standard and the dye under examination being always performed side by side.

4. In order to exhaust the bath as much as possible, the quantity of dye employed must not be too great in comparison with the amount of fabric to be dyed; furthermore, lighter colours are obtained which are more easily judged.

The materials on which the colours are produced are the following:—

Cotton, generally in the form of skeins, also frequently as woven strips, rarely as loose threads. When mordant dyes are being tested, it is advantageous to use the above-mentioned calico strips printed with different mordants (so-called alizarin strips).

Wool, most suitably in the form of so-called zephyr yarn, also frequently as flannel strips.

Silk, in the form of skeins.

The necessity also occasionally arises of dyeing on mixed materials; for example, half-silk, or on other materials, such as jute, china-grass, etc.

For every series of trials, equal weights, for example about 5 g., of the selected material—that is, equally heavy skeins or strips—are taken. The strips are labelled by cutting little holes at the ends, the skeins by twine with different numbers of knots. From 0.1 to 1 g. of the dye under examination is also weighed out, dissolved in hot water, and the solution diluted to 100 c.c. Sometimes, but not often, alcohol must be used as the solvent. Similar solutions of the type and of any other samples are prepared.

The experiment can be continued in slightly different ways, according to the purpose in view.

If the sole object is the selection of the best from several products offered for purchase, equal weights of the fabric are dyed with amounts of the different samples inversely proportional to the price; for example:—

1 g. of a sample at 9d.		0.9 g. of a sample at 10d.
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The trial which yields the best result naturally decides which is the cheapest article, whatever the price may be.

In another method, equal volumes—for example, 10 c.c. of the solutions of the sample under examination on the one hand and of the type on the other—are placed in dyeing-baths, containing the material which has previously been uniformly soaked. Even before the dyeing is finished, considerable differences of strength can be detected with a little care. If such exist, measured quantities of its dye-solution are added to the weaker bath until both colours have exactly the same strength at the end of the trial. In making the comparison, both skeins must be withdrawn simultaneously from the baths, otherwise their different degrees of moistness render it very difficult to form a correct judgment. The skeins are afterwards washed in water, dried, and once more carefully compared, since very slight differences are frequently only discernible when the skeins are dry.

Accurate results will usually be obtained most rapidly by the following method, especially when many samples, probably of different intensity, have to be examined simultaneously:—Several shades, of varying but exactly known strengths, are produced by means of the type. For example, three weighed skeins are dyed with sufficient type solution to produce a 1 per cent., 1.5 per cent., and 2 per cent. shade. As a rule, it is not difficult to make solutions of the samples of such strengths that accurately measured volumes, in their respective baths, produce shades of the same intensity as one or other of the three type shades. Even if a match is not secured, the experiment has, at all events, given approximate values, which must not, however, be regarded as final. According to their intensity, the sample shades lie between the 1 per cent. and the 1.5 per cent., or between the 1.5 and the 2 per cent. type shades, or outside these limits—that is, they are weaker than the 1 per cent. or stronger than the 2 per cent. type shade. Utilising the knowledge thus obtained, a new experiment is undertaken. Suppose, for example, that the shade produced by one of the samples is stronger than the 1.5 per cent. and weaker than the 2 per cent. type shade. Two skeins are again dyed with the type to the same intensities (1.5 per cent. and 2 per cent.); from the sample under examination one, or, better, two shades are produced, using in the latter instance, in the one case rather more, in the other rather less, of the dyeing solution than was employed in the first experiment. With a little practice, the proportions can be so selected that the results of the second experiment render an accurate judgment possible. If this is not the case, a third experiment must be performed, taking into account the information already obtained.

A considerable amount of experience, and, above all, a very sensitive eye for colour, are requisite for the accurate comparison of two shades.

With the aid of these attributes differences of intensity of 1 to 2 per cent. can be detected in the case of some dyes. Moreover, with practice, the eye becomes so sensitive to differences of intensity, that not more than two experiments are required to secure the correct proportions in the preceding operations. Also, the experimental error depends very largely on the nature of the dye, thus it is greatest in the comparison of pure yellow dyes. Again, large errors are easily introduced when the dyes differ from one another in purity and shade.

The purity and the more delicate differences of shade can be accurately judged only by comparison with dyeings of exactly the same strength, since the shades of many dyes vary with the intensity of the dyeing to such an extent that the omission of this precaution easily leads to large errors. Thus strong shades of yellow dyes appear redder than weaker shades, etc.

In forming a judgment, the comparison of the dye patterns must always be effected under the same conditions of lighting.

It is generally very difficult to value those dyes which do not "exhaust," *i.e.*, of which, in dyeing, a portion always remains in the bath. In such cases the following procedure is adopted:—After the completion of the dyeing operation, strips of white filter paper or white calico are immersed in each bath, removed, allowed to drain, and dried, and the colours of the paper or calico are compared. The use of so-called "exhausts" is more trustworthy. For this purpose, after the dye-bath has been only partly exhausted, a second dyeing operation (and a third if necessary) is performed on the same weight of fresh fibre, under the same conditions as in the first experiment. These second (or third) weaker colours (exhausts) are compared with one another.

Intermittent dyeing often gives valuable information as to the possible presence of more than one dye, of foreign substances, or of impurities. A piece of material, insufficient to exhaust it, is placed in the dye-bath, then a second piece, and so on, until the bath is completely exhausted. If the dye is pure, the various pieces have the same shades, even if they differ in intensity. (A judgment is only possible by the trained eye. See above.)

It would be out of place to mention fully the many precautions which must be observed in dyeing different fabrics with the numerous members of the coal tar dyes. The following details will provide sufficient general guidance for the satisfactory performance of most experiments:—

**Dyeing on Silk.**—As a rule, "boiled off" silk is used in dye trials, and in an unmordanted condition, since most dyes directly colour this material. It is always soaked before being introduced into the dyeing bath. Usually a bath of water, to which acetic or sulphuric acid has been added, suffices. Sometimes "bast soap" (one-sixth to one-third

of the volume of water), the liquid obtained in the process of boiling silk to remove the gum, and consisting of a solution of sericin and Marseilles soap, is used. Its addition to the dye-bath prevents too rapid dyeing and produces a more uniform colour, whilst at the same time the silk is brightened and acquires greater lustre. A measured quantity of the bast soap is first poured into the dyeing-vessel, and is warmed, then the necessary amount of acetic or sulphuric acid is added, after which the water and the dye solution are introduced in turn, and the liquid is thoroughly mixed. The silk skein is put in, repeatedly immersed, and withdrawn, the bath is heated to boiling and the skein introduced again, and the dyeing is completed by frequent immersion. Afterwards the silk is washed by repeated rinsing in a bath of water, which is replaced once or twice, and is finally "revived" in fresh water, which is very slightly acidified with acetic or sulphuric acid. After being repeatedly immersed, it is wrung out and dried.

Dyeing is effected in hot solutions in the case of most aniline dyes; the temperature being gradually raised to the boiling point. Many dyes, for example the eosins, give stronger shades when they are used at temperatures not so high as this. Certain dyes (magenta, methyl violet, etc.) are also used in neutral baths.

Only a few dyes are applied in the presence of fatty soaps. In such cases the bath is prepared by adding Marseilles soap to hot distilled water until a slight lather is produced. The silk is then dyed in the hot solution, washed thoroughly, and revived.

When testing alizarin and other mordant dyes, the silk must previously be suitably mordanted. In mordanting with alumina, the silk is placed, for example, in a bath of neutralised alum free from iron, immersed repeatedly, and allowed to remain in the mordant for about twelve hours; it is then wrung out, immersed for a short time in a cold solution of water-glass (sp. gr. 1.007), wrung out again, and, after being washed, is placed directly in the dye-bath, which contains one part of bast soap and five parts of water acidulated with acetic acid. The temperature is raised slowly to the boiling point and maintained there for one to one and a half hours; the silk is then rinsed, soaped, and revived.

In a quite analogous manner, silk is mordanted with chromium chloride, sp. gr. 1.162 (Badische Anilin und Soda fabrik), or with chrome mordant GA III., sp. gr. 1.162 (Farbwerke vorm. Meister, Lucius, und Brüning.)

**Dyeing on Wool.**—Generally skeins of zephyr yarn or flannel strips, in a thoroughly clean state (free from fat), are used. The material is soaked in luke-warm water, removed, and replaced in the bath after the addition of the dye-solution. It is repeatedly immersed while the bath is heated to boiling, and maintained at this temperature for

fifteen to thirty minutes. In the case of many dyes, it is more advantageous to perform the operation at a rather lower temperature.

Dyes which are effective in neutral baths can be employed alone or with 10 to 20 per cent. of sodium sulphate; acid dyes require an acid bath (5 per cent. of sulphuric acid and 10 to 20 per cent. of sodium sulphate or 10 to 15 per cent. of tartar substitute [sodium hydrogen sulphate]); the addition of alum or stannic chloride is often advantageous).

When mordant dyes are being used, the wool is boiled, as a rule, with 3 per cent. potassium bichromate and 2.5 per cent. potassium hydrogen tartrate, or 1 to 2 per cent. lactic acid, or with 4 per cent. chromium fluoride and 1 per cent. oxalic acid, for about one and a half hours, and, after being washed, is put in the tepid dye-bath. It is repeatedly immersed, whilst the temperature is slowly raised to the boiling point, and the liquid is boiled vigorously for about one and a half hours.

Boiling is unnecessary in the case of many dyes; the mordant (alum, potassium bichromate, chromium fluoride, etc., together with any auxiliary substances) is placed directly in the dye-bath (one-bath process).

**Dyeing on Cotton.**—Cotton is usually employed in the form of skeins. They should be thoroughly boiled and washed. Bleached material is requisite for clear, bright colours.

Substantive dyes (benzidine dyes) are dyed with the addition of 20 to 50 per cent. of sodium chloride or sodium sulphate, 5 per cent. of potassium carbonate, 5 per cent. of soft soap, 3 per cent. of curd soap, sodium carbonate, sodium phosphate, water-glass, or mixtures of these substances.

The cotton is put into the dye-bath at 50°—60°, and repeatedly immersed while the bath is being brought to the boiling point during the course of a half to one hour; it is then wrung out and dried. Frequently before drying it is washed, often it is soaped, and in many cases it is treated with solutions of copper sulphate or potassium bichromate.

Sulphide dyes are employed in a hot, alkaline bath (sodium sulphide, sodium hydroxide, with sodium chloride, sodium carbonate, etc.).

For use with basic dyes the cotton must be mordanted with tannin. For this purpose, the skeins are agitated for a short time in a 2 to 5 per cent. solution of tannin at 50°—70°, and are allowed to remain in the mordant for about six hours (best overnight); then they are again agitated and afterwards manipulated for about fifteen minutes in a tepid bath of 2 to 3 per cent. tartar emetic.

The thoroughly washed material is dyed in a luke-warm bath for thirty to forty-five minutes.

**Mordanting with Alumina.**—The cotton is agitated in a solution of basic aluminium sulphate, kept in the bath for about five hours, wrung out, and twenty minutes afterwards is passed through a tepid solution of sodium carbonate, water-glass, or sodium phosphate; it is then thoroughly washed and dyed in the luke-warm dye-bath, the temperature of which is slowly raised to  $90^{\circ}$ – $95^{\circ}$  during an interval of one to one and a half hours. After thorough washing, the cotton is frequently revived, for example, in a soap bath.

**Mordanting with Chromium.**—The skeins are placed in chromium chloride (sp. gr. 1.162) for four hours, wrung out, washed, and dyed. The operation is repeated for dark shades.

In another method the skeins are kept for twelve hours in the mordant GA I. (Farbwerke vorm. Meister, Lucius, und Brüning) and after being untwisted are placed for thirty minutes in a solution of 30 g. of sodium carbonate in 1 litre of water at  $60^{\circ}$ ; they are then washed and dyed.

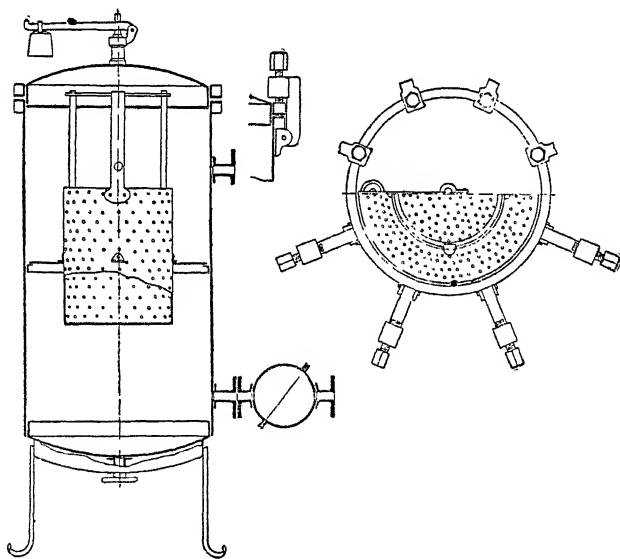


FIG. 144.

True mordant dyes, such as alizarin, etc., are generally sparingly soluble, and only remain in suspension in the dye-bath. They must always be employed in quite neutral or faintly acid (acetic acid) baths, and the alkalinity of the water must, for this reason, always be previously neutralised by acetic acid. When mordant dyes are being used, the above-mentioned strips streaked with different mordants (alizarin slips) are very often employed. The actual dyeing is effected by prolonged boiling.

### Print-Trials.

These are always counterparts of the methods employed in the large scale. Only the general principles can here be stated.

In calico printing, dyes are used which form insoluble lakes with either tannin or metallic oxides. Such are basic dyes and the true mordant dyes (alizarin, oxazines, etc.).

The former are treated with dilute acetic acid and tannin or with tannin-tartaric acid—that is, a solution of 50 parts of tannin and 5 parts of tartaric acid in 50 parts of water—and are mixed with a thickening material; in the case of true mordant dyes, the tannin is

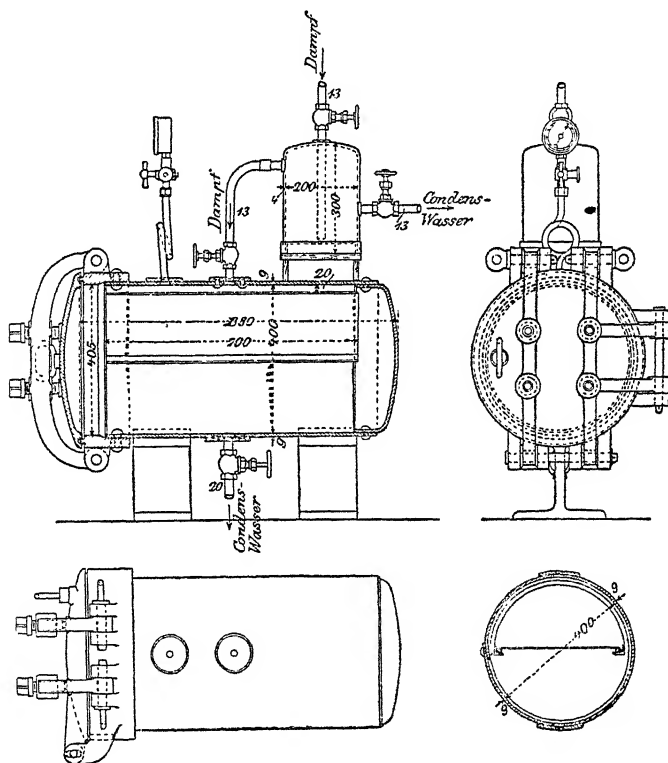


FIG. 145.

replaced by the acetate of aluminium, chromium, or iron (or also aluminium thiocyanate).

After being printed, the fabric is dried and steamed. Small vertical or horizontal copper or sheet iron boilers (Figs. 144 and 145) are used as steaming apparatus when the sample cannot be treated along with the goods.

The steaming removes not only the acetic acid which has been added, but also that present in the metallic acetate. As a result, the



dye forms a lake with the tannin or with the residual metallic oxide, and is thereby fixed on the fibre. After being steamed, the fabric is washed and soaped at about 50°.

Before being washed, materials mordanted with tannin are placed in a bath of tartar emetic at 60° (5 to 10 g. of tartar emetic in 1 litre of water).

As in dyeing, so also in printing, a type is employed in the examination; the sample-prints are compared with one another. The shade and purity can generally be judged with sufficient accuracy, but only by long experience and under suitable conditions can the comparison of the strengths be ascertained with the requisite degree of certainty. If the results do not afford an adequate guarantee of trustworthiness, it is better to attempt to decide the matter by dye-trials.

Flannel, in a thoroughly clean condition, is employed for print-trials on wool. Before printing, the flannel is "chlorod"—that is, passed through a dilute bath of bleaching powder or sodium hypochlorite and subsequently through dilute acid; it is then washed well, dried, and printed.

In many cases the wool is made ready by a solution of sodium stannate and subsequent treatment in an acid bath, or by aluminium acetate.

The printing material consists of the thickened solution of the dye and a little acetic or tartaric or oxalic acid. In the case of true mordant dyes (for example, alizarin) the suitable metallic mordant must of course be added.

The fixing is effected by steaming, generally without pressure.

Silk is printed directly with the thickened solution of the dye, containing a little free acid.

### Tests of Fastness.<sup>1</sup>

In addition to the examination of their strengths, dyes have frequently to be tested as to their fastness, on the fibre, to the action of water, alkalis, acids, sunlight, etc. This can be done as follows:—

*Fastness to Water.*—For this and the following tests, it is best to use yarn or other loose fibrous material. This is interlaced with undyed yarn and the plait is kept in water for some time, preferably overnight. The water should not become coloured and the undyed yarn in the plait should remain white.

*Fastness to Soap or Washing.*—A similarly prepared plait is agitated for about fifteen minutes in a soap-bath (0.5 to 1 per cent. solution of Marseilles soap), at 50°—60°. If the dye withstands this treatment well, the experiment is repeated in a boiling soap-bath. Dyes to be

Cf. also H. Lange, "Testing for Fastness, etc.," *Färber-Zeit.*, 1903, 14, 269; G. v. Georgievics, "How should Dyes be Tested for Fastness," *Z. Farb. Ind.*, 1902, 1, 656.

used for calico printing must be able to bear prolonged soaping at about  $60^{\circ}$  without appreciable effect.

When unspun cotton, intended for the manufacture of half-wool tissues, is to be tested, it is mixed with white wool by means of hand carding-combs and placed in a warm, approximately 0.5 per cent. solution of soft soap at  $50^{\circ}$  for fifteen to thirty minutes. It is then well washed, and the condition of the wool, the cotton, the soap solution, and the washing water is examined.

*Fastness to Milling* is of special importance for dyes which are used in dyeing the loose wool employed in cloth manufacture. The property is exhibited almost only by true mordant dyes.

The process of milling consists in scouring and kneading the wool with soap solution, whereby the wool fibres become felted. In this process, the dye must not be appreciably eliminated from the material, and also the white wool, which has been mixed with the dyed fibres, must not become coloured.

Loose dyed wool is the best material for the milling test. It is plaited with white wool and vigorously kneaded with soap solution for some time. (The soap solution contains 0.5 to 1 per cent. of soft soap with or without the addition of sodium carbonate, fuller's earth, and such like.) The lather obtained ought not to be appreciably coloured. The plait is then washed thoroughly with water, laid on wet filter-paper, and allowed to dry as slowly as possible. The white wool ought not to be coloured, or only very slightly. Such colouring of the white wool is termed "bleeding" of the dye. This phenomenon generally appears only after the soap has been completely removed by washing. Absence of bleeding is a property chiefly of dyes which are fixed by metallic mordants, and, moreover, is usually exhibited only by chromium lakes. It must be remembered that milling on the large scale, as a rule, is more effective than is possible on the small scale; it is well, therefore, in important cases, to mill the sample with a batch of goods in the works.

*Fastness to Alkali*.—The skein of cotton is interlaced with undyed cotton and the resulting plait is placed in a tepid 1 to 3 per cent. bath of sodium carbonate for half to one hour. Any change which occurs is often noticeable even when the plait is wet, sometimes only after it has been washed and dried.

Wool is placed in ammonium hydroxide of different concentrations, and is carefully examined while wet and also after drying.

In another process it is saturated with a 5 per cent. solution of sodium carbonate, and examined after being dried.

*Fastness to Bleaching*.—Wool and silk are suspended for a few hours in the sulphur chamber, or placed for a day in dilute aqueous sulphurous acid; in both cases they are washed and dried.

In some cases it is also necessary to examine the effect produced by a dilute solution of hydrogen peroxide.

Cotton is placed in a solution of bleaching-powder of sp.gr. 1.001-1.003, washed after half to one hour, passed through a bath of very dilute sulphuric acid (sp. gr. 1.005), washed thoroughly, and dried.

*Fastness to Rubbing* is tested by vigorously rubbing the dyed samples on white calico or coarse white paper; the intensity of the colour of the rubbed surface can then be judged, especially if a dye of known fastness to rubbing is used in a comparative experiment.

*Fastness to Perspiration* can be satisfactorily judged only by testing the material under the conditions of everyday life. (Wearing of underclothing which has been dyed with the substance under examination.)

If this is not done, a more or less satisfactory test is obtained as follows:—The dyed sample is kneaded with dilute acetic acid (about 0.5 per cent.), dried, and submitted again to the same treatment. If the colour suffers any change it will certainly not be fast to perspiration.

In testing for fastness to perspiration E. Davidis,<sup>1</sup> holding the opinion that human perspiration contains ammonium hydroxide and neutral fats, recommends, in the case of dyed woollen goods, the replacement of the acetic acid process by an alkaline method, in which the material is treated with a solution of ammonium hydroxide and soap. The solution consists of—

5 g. Marseilles soap,  
3 c.c. ammonium hydroxide,  
1 litre of water,

and is used at 50°. The material under examination is kept in this solution for ten minutes, and is frequently squeezed. Conclusions as to the degree of sensitiveness of the material to perspiration can often be drawn from the more or less pronounced colour of the liquid. The thoroughly squeezed but unwashed sample is then laid on a piece of muslin and dried with a flat-iron. The degree of fastness of the dye to perspiration is then ascertained by the bleeding of the dyed material and the colour of the originally white muslin.

A very good and much more searching test is the following:—The material is thoroughly squeezed and rolled, together with a strip of white calico, tightly round a glass rod. The bundle is allowed to dry at 50°. In consequence of the prolonged drying the dye has much more time to spread into the surrounding material or the white calico than is the case when the drying is rapidly accomplished by a flat-iron.

<sup>1</sup> *Färber-Zeit.*, 1904, 15, 373.

*Fastness to Ironing* is tested by means of  $\frac{1}{2}$  hot flat-iron. The colour should remain unchanged, or, at any rate, should recover its original appearance after the material has been exposed to the air for a short time.

*Fastness to Hot-pressing*.—A sample is exposed to the action of superheated steam at about  $110^{\circ}$ ; or it is steamed, if possible, with a piece which is to be treated on the large scale. ••

*Fastness to Light (Fastness to Weather)*.—As a rule, the expert means by the term "fastness to light" stability not only to light and air, but also to the action of heat, moisture, dust, and any possible acid or alkaline constituents of the last. On this account, it is advisable not to perform the test exclusively behind glass.

The samples under examination (skeins or strips) are fastened side by side (and, preferably together with samples of known fastness) to a clean, smooth, polished board or pasteboard, and are about half covered with a piece of paper or cardboard; in this state they are freely exposed to the action of light, air, etc. The time of exposure and the atmospheric conditions (whether any sunshine or rain, and, if so, how much) are noted and the samples are carefully examined from time to time for any alterations. To obtain trustworthy results it must be remembered that fastness to light depends on the strength of the dye; weak colours are less resistant than strong. For this reason only samples of equal colour intensity should be exposed together. Moreover, the dyed materials under comparison must be simultaneously exposed side by side and not one after another, because, as has been shown by Bunsen and Roscoe, the chemical activity of daylight not only varies during the day, but is different at different times of the year. A dyed material often requires a three or four times longer exposure in winter than in summer, to produce an equal degree of fading. Finally, it cannot be assumed that the results obtained in the case of one fabric are equally true for other fabrics. As a rule, colours prepared from one and the same dye are least fast on paper, then follows cotton, whilst wool and silk retain the colours best of all. Exceptions to this generalisation, are, however, known.<sup>1</sup>

The degree of fastness to light which is required of the various dyes varies very much, and standards should be chosen which correspond with the use to which the dye is to be applied.

For the testing of fastness to light, A. Scheurer and A. Brylinski<sup>2</sup> employ standards of vat-dyed cotton of three intensities. The fading of these in sunlight is compared with that simultaneously occurring in

<sup>1</sup> Kitschelt, *Z. angew. Chem.*, 1897, 10, 100; cf. also *Chem. News.*, 1896, 74, 205, 210; Lehne, *Färber-Zeit.*, 1896-1897, 8, 138.

<sup>2</sup> *Bull. Soc. Ind. Mulhouse*, 1898, 68, 119, 273; 1899, 69, 93.

the samples under examination. The three stock standards are dyed in three gradations by indigo.

1st type.	A dark blue,	produced by 4 immersions,	contains 1.2 g. indigotin per sq. m.
2nd "	A mean "	" 2 "	" " 0.52 g. " "
3rd "	A pale "	" 1 " "	" " 0.25 g. " "

The dye under examination is also dyed in three strengths: *i.e.*, in dark, medium, and light shades. The exposure to light is done behind glass, using Marchand's apparatus, and is prolonged, in the first instance, until type 3 (the pale indigo blue) has faded to half its strength. If the eye cannot detect any change in the palest sample under examination, the exposure is continued until type 2 (mean indigo blue) has lost half its strength, and so on.

Dyes are termed very fast when they are more resistant than type 1 (dark indigo blue); fast when they behave in sunlight like type 1 (dark indigo blue); half-fast when they behave like type 2; slightly fast if like type 3; not fast when they are less resistant than type 3.

Moreover, a determination has been made of the relations between these different degrees of fastness and the amount of indigo decomposed by the exposure of 1 sq. m. of "mean indigo blue" (type 2). The sample, after its colour had faded to half its strength, suffered a loss corresponding with 0.25 g. of indigotin per sq. m. The amount of indigotin was estimated by extraction with glacial acetic acid according to Brylinski's method (see below).

Finally, it has been ascertained that 0.1 g. of decomposed indigotin (per sq. m.) corresponds with 312 to 318 c.c. of carbon dioxide (reduced to 0° and 760 mm.), which are evolved per sq. cm. by exposure in a Marchand apparatus (and are produced by the action of the light on ferric oxalate).

If these last results have more than a relative value, it should be possible to express the magnitude of the actinic activity in terms of the amount of indigotin decomposed per sq. m. or of the number of c.c. of carbon dioxide evolved per sq. cm. through the exposure to the light.

At the instance of the Bayer Company, M. Kitschelt<sup>1</sup> has undertaken a comparative examination of the behaviour of all wool dyes on exposure to light, the standard of reference being a new unit of the bleaching power of light. This unit is the interval of time required for the disappearance of the colour of a 2 per cent. dyeing of thiazol yellow on cotton. Thiazol yellow is more suitable than other dyes for this purpose, because it fades uniformly to whiteness and possesses a suitable degree of sensitiveness to light.<sup>2</sup>

<sup>1</sup> *Leipziger Monatsschrift f. Text.-Ind.*, 1904, 19, 21, 100.

<sup>2</sup> *Cf.* also Bolis, *Rev. Gen. Mat. Col.*, 1908, 12, 289.

### Colorimetry.

It has been already mentioned that those methods of examination, by which the strength of dyes are estimated by comparisons of the intensities of the colours of their solutions, are, as a rule, not applicable in practice. Nevertheless, in special cases, for example in provisional, classifying trials, a colorimeter can be usefully employed; for this reason a few suitable instruments will be now specified.

The different forms of the apparatus which are made are all the same in principle. A solution of known strength serves as the standard, and the solution of the dye under examination is compared with it. The intensity is determined either by adding water or alcohol to a measured volume of the solution under examination until its colour is the same as that of the standard solution, or by varying the depth of the liquid, through which the operator is looking, until again the colour is the same as that of the standard solution. The quantities of dye, present in two different solutions of the same intensity, are proportional to the volumes of the solutions.

Very dilute solutions of the dyes must be used in the comparison in order that slight differences of intensity may be detected. Two similarly graduated burettes of the same diameter are used in the experiment. Equal volumes, for example, 50 c.c. of the two solutions (one of the type, the other of the dye under examination) are placed in the burettes, which are then so arranged that the experimenter can look from above downwards through the two columns of liquid. The solution which has the darker colour is carefully run out until both columns of liquid have exactly the same intensity. The heights of the liquids in the burettes are now read; the colour strengths of the two solutions are inversely proportional to these heights.

The procedure with Houton-Labillardière's and with Salleron's colorimeters is quite analogous. Of a somewhat different kind are Collardeau and Mills's colorimeters, A. Müller's complementary colorimeter, and Lovibond's tintometer.<sup>1</sup> The last serves for measuring and recording dyeings, and is intended specially for providing colours of definite shades and definite depths.

For other colorimeters, cf. Vol. I., pp. 379, 758, and 766, and this Vol., p. 249.

<sup>1</sup> *J. Soc. Dyers and Col.*, 1887, 3, 186; 1908, 24, 36.

COMPOSITION OF THE MORE IMPORTANT COMMERCIAL DYES<sup>1</sup>

## I. NITRO-COMPOUNDS

**Picric Acid** (Trinitrophenol),  $C_6H_2(NO_2)_3 \cdot OH$ .

Picric acids prepared by treating phenolsulphonic acid with concentrated nitric acid. In the pure state it forms pale yellow crystals, which are moderately sparingly soluble in cold water, but dissolve easily in hot water, alcohol, or ether. It melts at  $122^{\circ} \cdot 5$ . Marchand states that picric acid dissolves in:—

166	parts of water at	$5^{\circ}$
86	" "	$15^{\circ}$
73	" "	$26^{\circ}$
26	" "	$73^{\circ}$

The acid and also its salts are characterised by an intensely bitter taste. Picric acid dyes wool and silk in acid solution a greenish yellow. Formerly it was extensively employed in dyeing for the shading of green and red, and also for the production of mixed colours.

**Martius Yellow** (Naphthol Yellow, Manchester Yellow, Jaune d'or).—This dye is the sodium, ammonium, or more rarely the calcium salt of binitro- $\alpha$ -naphthol, and is prepared by boiling diazonaphthalene or  $\alpha$ -naphthol-2:4-disulphonic acid with dilute nitric acid.

The pure free binitronaphthol, melting point  $138^{\circ}$ , forms sulphur-yellow crystals which are sparingly soluble in water, rather more readily in alcohol, ether, or glacial acetic acid. It yields with alkalis golden yellow salts which crystallise well and are easily soluble in hot water. Solutions of binitronaphthol do not taste bitter. In slightly acidified solution the substance dyes wool and silk a beautiful golden yellow shade; its use, however, has been diminished since the discovery of much more stable azo dyes. It sublimes easily and can be removed from the fabric by warming.

**Naphthol Yellow S** is the potassium or sodium salt of 2:4-binitro- $\alpha$ -naphthol-7-sulphonic acid,  $OH \cdot C_{10}H_4(NO_2)_2 \cdot SO_3H$ , and is prepared by treating  $\alpha$ -naphthol-2:4:7-trisulphonic acid with dilute nitric acid at  $25^{\circ}$ .

The free acid forms long, yellow needles, which are easily soluble in water. It is a strong, dibasic acid; the potassium salt, in particular, is characterised by its sparing solubility. Like picric acid, it can displace mineral acids from their potassium salts. The commercial product is a pale yellow, crystalline powder. It is very sparingly

<sup>1</sup> A full and uniform description of the numerous commercial dyes is impossible within the scope of this work. The following account is accordingly restricted to those dyes which are of special importance and interest.

soluble in cold water, but comparatively easily in hot. The salts of the sulphonic acid possess the advantage over Martius yellow of not being precipitated by acids and can be more easily employed in dyeing. Moreover, the colours produced are faster.

It dyes wool in an acid-bath, and silk in an acidulated boiled-off liquor-bath.

## II. AZO DYES.

The azo dyes comprise a well-defined group of substances which have attained considerable importance in all branches of dyeing. The members first prepared were of a basic character, but in course of time numerous acid dyes have been produced which differ from the former by their greater stability and more extensive applicability.

In the examination of azo dyes attention must be paid to their behaviour towards reducing agents and towards concentrated sulphuric acid. Many are converted by careful reduction into most easily oxidisable hydrazo-compounds; vigorous reduction causes fission, which in many cases may furnish valuable evidence for the recognition of the dye and the determination of its constitution. Azo dyes give characteristic colorations when dissolved in concentrated sulphuric acid.

For the estimation of azo dyes (and of nitro-compounds, for example, picric acid and naphthol yellow S) E. Knecht<sup>1</sup> recommends the use of titanium trichloride, the preparation of which, from the commercial product, for this purpose is described in detail. Titanium trichloride quantitatively reduces azo-dyes, the azo group being eliminated. Permanent decolorisation is produced. Four molecules of the trichloride correspond with one azo-group. The boiling solution of the dye, strongly acidified with hydrochloric acid, is titrated with standard titanium trichloride in a current of carbon dioxide until the colour disappears. In the case of many azo dyes, particularly of those derived from benzidine and similarly constituted bases, the reduction is evidently retarded by the insolubility of the dye, and the end-point is not easily detected. In such cases it is advisable to add an excess of standard titanium trichloride to the boiling solution of the azo dye, in a current of carbon dioxide, and, after cooling, to titrate the excess with standard ferric alum. This method yields valuable information for many purposes; it does not, however, furnish any evidence of purity and shade. As a rule, its application in dye trials is not omitted on this account.

### I. Aminoazo-Compounds.

**Aminoazobenzene**,  $\text{C}_6\text{H}_5 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ , as such, was used only for a short time as a yellow dye; it is extensively employed, however,

<sup>1</sup> *Ber.*, 1903, 36, 166, 1549; *J. Soc. Dyers and Col.*, 1905, 21, 3.



in the production of other dyes, such as fast yellow, tetrazo dyes, indulines, etc.

It crystallises in golden yellow needles and leaflets, which melt at  $127^{\circ}$  and distil at a higher temperature with partial decomposition; it dissolves slightly in water, easily in alcohol and benzene. It combines with acids to form salts which crystallise well but are very unstable. They usually possess a steel-blue reflex, and dissolve only sparingly in acidified water. They are decomposed almost completely by pure water. The acid solution has a fine red colour. The nitrate and the hydrochloride are fairly soluble in alcohol, the sulphate is sparingly soluble. Concentrated sulphuric acid and hydrochloric acid dissolve aminoazobenzene, forming yellowish brown solutions which become red on dilution with water. Reducing agents, such as hydrochloric acid and zinc dust or tin, convert aminoazobenzene into aniline and *p*-phenylenediamine. Nitrous acid changes it into diazoazobenzene.

**Chrysoïdine** (Diaminoazobenzene),  $C_6H_5 \cdot N_2 \cdot C_6H_3(NH_2)_2$ , is produced by mixing a dilute solution of diazobenzene chloride or sulphate with a dilute solution of *m*-phenylenediamine.

The free base forms beautiful, yellow needles, melting at  $117^{\circ} \cdot 5$ , which are almost insoluble in cold water, sparingly soluble in hot water, and easily soluble in alcohol or ether. It combines with 1 mol. of an acid to form stable salts, the solutions of which have a fine yellow colour. The hydrochloride crystallises either in glistening, black octahedra or in slender, felted needles.

The solution of the mono-acid salt acquires a beautiful red colour by the addition of an excess of mineral acids, just as in the case of aminazobenzene. The resulting di-acid salts are very unstable and cannot be obtained in the solid state.

Chrysoïdine is a very strong, beautiful, yellow dye, which unfortunately is not particularly fast to light and air. It dyes directly on wool and silk in neutral baths. Unmordanted cotton also can fix a certain amount, but requires a previous treatment with tannin in order to acquire a good colour.

**Chrysoïdine R** is similarly prepared from diazobenzene chloride and *m*-tolylene-diamine. It dyes in redder shades.

**Bismarck Brown** (Vesuvine, Phenylene Brown, Manchester Brown) is prepared by the action of sodium nitrite on a solution of *m*-phenylenediamine hydrochloride. The dye is precipitated with sodium chloride and is purified by repeated solution and precipitation. It consists of the dihydrochloride of triaminoazobenzene or of the compound  $C_6H_4[N_2 \cdot C_6H_3(NH_2)_2]_2 \cdot 4HCl$ , or both. It is a strong, yellowish brown dye, which is applied in dyeing wool, silk, cotton, and leather. The process of dyeing is similar to that of chrysoïdine.

**Acid Yellow** (Fast Yellow) consists of a mixture of the sodium salts of aminoazobenzenesulphonic acid and aminoazobenzenedisulphonic acid, and is prepared by the action of fuming sulphuric acid on aminoazobenzene or one of its salts. According to the strength of the acid, the duration of the reaction, or the temperature, the product may consist chiefly of the mono- or of the di-sulphonic acid, both of which are precipitated on dilution with water.

In general the sulphonic acids give the same reactions as aminoazobenzene; they are coloured red by dilute acids, yellowish brown by concentrated acids. Fast yellow dyes wool and silk in a faintly acid bath. It is not employed for dyeing cotton. The higher homologues of aminoazobenzene—for example, aminoazotoluene—are yellow dyes which have a redder tint. Fast yellow is used in dyeing mostly as a shading material. Further, the aminoazobenzenesulphonic acids constitute the starting point for the production of Biebrich scarlet and other disazo-dyes.

**Orange IV** (Diphenylamine Orange, Tropaeolin OO) is prepared by allowing a thin paste of diphenylamine hydrochloride containing free acid to flow into a solution of diazobenzenesulphonic acid. After being washed, the precipitated acid is converted into the sodium salt. The sulphonic acid consists of violet needles, which are sparingly soluble in water. The sodium salt forms leaflets which are sparingly soluble in cold, easily in hot water. Its solution is coloured reddish violet by acids, and deposits glistening needles of the sulphonic acid even at moderately great dilutions. The calcium salt is quite insoluble. The sodium salt constitutes the technical product. Orange IV is a very fine, strong dye, the shade of which is yellowish orange. Like most acid colouring matters it is dyed from a dilute sulphuric acid bath.

Of the different isomerides and homologues of Orange IV which are found in commerce, **Metanil Yellow** is prepared from diazobenzene-*m*-sulphonic acid, and diphenylamine. It closely resembles the preceding dye in its reactions, but differs from it in its yellower shade and in the greater solubility of its salts. **Fast Yellow N** is prepared from diazotised *p*-toluidinesulphonic acid and diphenylamine. It differs from the preceding in that it develops with concentrated sulphuric acid a green colour, which changes to violet on dilution with water. Orange IV and Metanil Yellow give a violet solution in sulphuric acid.

**Curcumeine** (New Yellow, Citronine, Citronine NE, Azoflavine 3 R ex. conc.) is prepared by the moderate nitration of Orange IV and **Azo Acid Yellow** (Azo Yellow, Azoflavine, Indian Yellow, Azo Yellow, 3 G ex. conc, Citronine, 2 AEJ) by more vigorous nitration,

They are mixtures of nitrated Orange IV with nitrodiphenylamine (P. Juillard).<sup>1</sup>

**Orange III** [Tropaeolin D, Helianthin, Methyl Orange (the sodium salt of dimethylaminoazobenzenesulphonic acid)] is very seldom brought on the market as a dye. Its application as an indicator is mentioned in Vol. I., pp. 61 *et seq.* Its great sensitiveness to acids prevents its application as a dye. It dyes wool and silk best in the presence of alum or stannic chloride, and produces an orange shade.

The free sulphonic acid forms reddish violet needles with a steel-blue reflex, and dissolves sparingly in water giving a red solution. With sulphuric acid it gives a yellowish brown colour, which is changed to red on dilution. The sodium salt forms beautiful, golden yellow leaflets which dissolve easily in hot water giving an orange-yellow solution. The solution is turned red even by a trace of a mineral acid. The dye is converted into sulphanilic acid and dimethyl-*p*-phenylenediamine when its acidified solution is treated with zinc dust. The dimethylated diamine can be detected very easily by the methylene blue reaction.

**Archil Substitute V** is produced by the combination of *p*-nitrodiazobenzene and naphthionic acid. The commercial product is a brown paste, consisting of the sodium salt. It forms a reddish brown solution in water, and dyes wool archil red from an acid bath. Its chief merit lies in its remarkable equalising property.

The aqueous solution yields a brownish red precipitate on the addition of hydrochloric acid; the dye dissolves in concentrated sulphuric acid to a magenta-red solution.

**Apollo Red** is obtained from *p*-nitrodiazobenzene and  $\alpha$ -naphthylaminedisulphonic acid D, and is a brown powder which forms a brownish red solution in water. Hydrochloric acid develops a magenta-red coloration and sodium hydroxide produces a brown precipitate which is soluble in water; concentrated sulphuric acid gives a magenta-red solution. Wool is dyed an archil red from an acid bath.

**Wool Violet S** is obtained from 2:4-dinitrodiazobenzene and diethylmetanilic acid. The commercial product is a black powder, which dissolves in water and in alcohol with a reddish violet colour. The colour of the solution is changed to orange by hydrochloric acid. Sodium hydroxide produces a bluish violet precipitate; in concentrated sulphuric acid a scarlet-red solution is formed. Wool is dyed reddish violet from an acid bath.

**Meta Chrome Brown B** (*Akt. Ges.*) is prepared from diazotised picramic acid and *m*-tolylenediamine.

**Anthracyl Chrome Green** (*Dahl*) is obtained from diazotised picramic acid and naphthionic acid. It dissolves in water with a reddish brown colour. Hydrochloric acid gives a blue-red colour and a

<sup>1</sup> *Bull. Soc. Chim.*, 1905 [iii.], 33, 974-987.

Bordeaux red precipitate. Sodium hydroxide gives a brown precipitate. Concentrated sulphuric acid gives a bluish fiery red solution,

**Palatine Chrome Brown W** (*B.A.S.F.*) is prepared from diazotised *o*-aminophenol-*p*-sulphonic acid and *m*-phenylenediamine. Its solution in water is orange brown, and in sulphuric acid dark orange brown.

## 2. Hydroxyazo-Compounds. ••

**Tropaeolin O** (Resorcin Yellow, Chrysoin) is the sodium salt of *p*-sulpho-benzeneazoresorcinol and is obtained by adding a solution of *p*-diazobenzenesulphonic acid to a slightly alkaline solution of resorcinol.

The free acid forms blackish brown leaflets with a green reflex, which are slightly soluble in cold, moderately so in hot water. Concentrated sulphuric acid dissolves it with a yellow colour. The sodium salt forms beautiful, orange-yellow leaflets, or large prisms. The acid is not precipitated from an aqueous solution of the sodium salt by the addition of dilute hydrochloric acid. The precipitation is only effected by a larger amount of concentrated hydrochloric acid or of dilute sulphuric acid. Tropaeolin O is a fine, very strong dye, the shade of which is rather yellower than that of Orange IV. The method of dyeing is the same for both.

**Phenoflavine** is prepared from *m*-diazobenzenesulphonic acid and 3-aminophenol-5-sulphonic acid (III), and is brought on the market in the form of the sodium salt, a brownish yellow powder which forms a yellow solution in water. The colour of the solution is changed to orange by hydrochloric acid or sodium hydroxide; concentrated sulphuric acid produces a yellow solution. Wool is dyed yellow from an acid bath.

**New Phosphine G**,  $\text{N}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{OH})_2$ , is obtained from *p*-diazobenzyl dimethylamine and resorcinol. The commercial product is a yellowish brown powder, which forms an orange-brown solution in water: hydrochloric acid renders the aqueous solution turbid, whilst sodium hydroxide turns it browner. Concentrated sulphuric acid forms a brownish orange solution. It resembles ordinary phosphine in its dyeing properties, but produces rather greener shades. It is employed in dyeing leather and tannin-mordanted cotton.

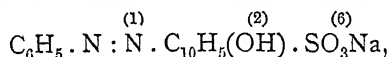
**Tannin Orange R**,  $\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{N}(\text{CH}_3)_2$ ,  $\text{HCl}$ , is prepared from *p*-diazobenzyl dimethylamine and  $\beta$ -naphthol. The commercial product is a reddish brown paste. It dissolves in distilled water forming an orange-brown solution; which gives a brown precipitate with ammonium or sodium hydroxides, soluble in acids. An excess of hydrochloric acid also produces a brown precipitate. Concentrated sulphuric acid colours the substance reddish violet.

✓ **Orange II** (Tropaeolin OOO No. 2,  $\beta$ -Naphthol Orange; Orange extra, Mandarin G extra; Gold Orange),  $\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{Na}$ .

—The sulphonic acid<sup>†</sup> is a vermillion powder which is easily soluble in hot water. Concentrated sulphuric acid dissolves it with a magenta-red colour which changes to orange on dilution. The sodium salt which constitutes the commercial product, crystallises from hot water in elongated, orange-yellow leaflets which contain water of crystallisation. The anhydrous salt is a scarlet powder. The orange-yellow colour of the solution is not affected by alkalis (distinction from  $\alpha$ -naphthol dyes). The calcium salt, produced by the addition of calcium chloride to the solution, is moderately soluble in hot water, although much less so than the sodium salt. The barium salt is almost completely insoluble.

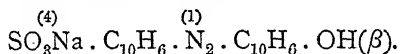
Orange II is a very important azo dye, characterised by its beauty and stability. It is extensively employed in dyeing, either by itself or for shading scarlet-red dyes. The method of dyeing is that of the acid azo dyes.

**Crocein Orange** (Brilliant Orange G, Ponceau 4GB),



is obtained from diazobenzene chloride and  $\beta$ -naphthol-6-sulphonic acid (Schaeffer's acid). The commercial product (the sodium salt) is a red powder which forms an orange-yellow solution in water; hydrochloric acid produces a brown precipitate; concentrated sulphuric acid gives an orange-yellow solution. Wool is dyed orange-yellow from an acid bath.

**Fast Red** (Roccellin, Rauracienne),



The free acid and the sodium salt form brown needles which are sparingly soluble in cold water, more easily in hot water. The solution has a brownish red colour. Concentrated sulphuric acid dissolves the dye with a bluish violet colour, which turns brown on dilution and the sulphonic acid is precipitated. The potassium salt is quite insoluble. Fast Red is a very strong dye, producing shades intermediate between those of scarlet and Bordeaux reds. Like the preceding, it is an acid dye.

**Brilliant Fast Red G<sup>1</sup>** (*B.A.S.F.*), obtained from diazotised  $\alpha$ -naphthylamine-5-sulphonic acid and  $\beta$ -naphthol, yields brilliant shades with a yellow tinge.

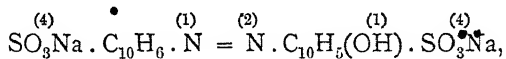
**Lithol Red** (*B.A.S.F.*), specially used in the lake industry, is prepared from  $\beta$ -naphthylamine-1-sulphonic acid and  $\beta$ -naphthol.

**Heliopurpurin 7BL** (*By*) is prepared from  $\beta$ -naphthylamine-1:6-disulphonic acid and  $\beta$ -naphthol-3:6-disulphonic acid (R). The **4BL**

<sup>1</sup> *Chem. Zeit.*, 1900, 24, ref. 115.

brand is obtained from  $\beta$ -naphthylamine-3:6-disulphonic acid and  $\alpha$ -naphthol-3:6-disulphonic acid, and the GL brand from  $\beta$ -naphthylamine-3:6-disulphonic acid and  $\beta$ -naphthol-3:6:8-trisulphonic acid. These dyes are also specially used for the preparation of lakes.

**Azorubin S** (Azo Acid Rubin, Carmoisin, Fast Red C, Nacarat, etc.),



is obtained by the action of diazonaphthalenesulphonic acid on  $\alpha$ -naphthol-4-sulphonic acid. The commercial product is a brown powder which forms a magenta-red solution in water. Concentrated sulphuric acid produces a violet solution which is turned magenta-red by the addition of water. Brown flocks are precipitated from the aqueous solution by hydrochloric acid; the colour of the solution is changed to yellow by sodium hydroxide. Wool is dyed red from an acid bath.

**Crocein 3BX**,  $\text{SO}_3\text{Na} \cdot \text{C}_{10}\text{H}_6 \cdot \text{N} : \text{N} \cdot \text{C}_{10}\text{H}_5(\text{OH}) \cdot \text{SO}_3\text{Na}$ , is obtained by the action of  $\alpha$ -diazonaphthalene-4-sulphonic acid on  $\beta$ -naphthol-8-sulphonic acid (crocein acid). It is a red powder which gives a yellowish red solution in water. Wool is dyed scarlet-red from an acid bath. It develops a reddish violet coloration with concentrated sulphuric acid.

**Double Brilliant Scarlet 3R** (Double Scarlet extra S) is produced from diazotised  $\beta$ -naphthylamine-6-sulphonic acid (Brönner's acid) and  $\alpha$ -naphthol-4-sulphonic acid. It is a brownish red powder, which dissolves in water with a yellowish red colour, gives a magenta-red solution in concentrated sulphuric acid, and dyes wool scarlet-red from an acid bath.

**Eosamin B<sup>1</sup>** is obtained from diazotised *m*-amino-*p*-cresol ethyl ether and  $\alpha$ -naphthol-3:6-disulphonic acid, and is a brownish red powder, which dissolves easily in water, forming a red solution. The colour of the aqueous solution is unchanged by hydrochloric acid and is darkened slightly by alkalis. The dye gives a bluish violet solution in concentrated sulphuric acid, which is changed immediately to rose-red on dilution with water. It dyes wool and silk from an acid bath.

**Guinea-Carmin B<sup>2</sup>** (*Akt. Ges.*).—A dark red powder which is sparingly soluble in cold water but dissolves readily in hot water giving a violet solution. Reddish blue flocks separate when the hot solution is cooled. The aqueous solution is rendered bluer by hydrochloric acid, and orange by sodium hydroxide. The dye forms a blue solution in concentrated sulphuric acid.

It dyes wool from an acid bath in bright red shades with a bluish tinge, which are moderately fast to acids, alkalis, and sulphur. It also

<sup>1</sup> *Chem. Ind.*, 1896, 19, 8.

<sup>2</sup> *Rev. Gen. Nat. Col.*, 1900, 4, 64.

equalises very well. For dyeing it is conveniently dissolved in acidified water (0.1 per cent. sulphuric acid). The dyeing must be performed in wooden vessels since copper and tin spoil the shade.

The  $\beta$ -naphtholdisulphonic acids yield numerous valuable dyes, of which the following should be mentioned, but it must be observed that the same dye is often put on the market by different manufacturers under different names.

**Ponceau 2G** is prepared from diazobenzene and R-salt (the sodium salt of  $\beta$ -naphthol-3:6-disulphonic acid). It dyes wool and silk reddish orange in an acid bath.

**Ponceau R** is obtained from diazoxylene (from crude xylidine) and R-salt.

**Ponceau 2R** is prepared from diazo-*m*-xylene and R-salt.

**Ponceau 3R** is prepared from diazoethyl-*m*-xylene and R-salt.

The shade of these three dyes is a beautiful scarlet-red; R is the yellowest and 3R the bluest product.

**Bordeaux B** is obtained from  $\alpha$ -diazonaphthalene and R-salt. It is rather sparingly soluble in water. Concentrated sulphuric acid produces a blue solution which becomes violet on dilution. The calcium salt is insoluble. It dyes wool bluish red with a tinge of brown.

**Amaranth** is produced by the action of diazo- $\alpha$ -naphthalene-4-sulphonic acid on R-salt.

G-Acid ( $\beta$ -naphthol-6:8-disulphonic acid) forms dyes the shades of which are much yellower than those produced from R-salt.

**Orange G**,  $C_6H_5.N:N.C_{10}H_4(OH)(SO_3Na)_2$ , is prepared from diazobenzene and  $\beta$ -naphthol-6:8-disulphonic acid. It dyes wool yellowish orange from an acid bath and gives an orange-yellow solution in concentrated sulphuric acid.

**Crystal Scarlet 6R** is obtained from  $\alpha$ -diazonaphthalene and G-salt. The commercial product consists of brownish red, glistening crystals.

**New Coccin** is obtained from  $\alpha$ -diazonaphthalene 4-sulphonic acid and G-salt.

**Palatine Scarlet** is prepared from diazo-*m*-xylene and  $\alpha$ -naphthol-3:6-disulphonic acid.

**Wool Scarlet R** is prepared from diazoxylene and  $\alpha$ -naphthol-4:8-disulphonic acid (Schöllkopf's acid), and is a brownish red powder which dissolves in water with a yellowish red colour. The colour of the aqueous solution is changed to a bluer red by hydrochloric acid. Concentrated sulphuric acid produces a cherry-red solution. It dyes wool red from an acid bath.

**Azo Bordeaux** is prepared from  $\alpha$ -diazonaphthalene and  $\alpha$ -naphthol-4:8-disulphonic acid. The commercial product (the sodium salt) is a brown powder, which forms a magenta-red solution in water. Hydrochloric acid and sodium hydroxide do not affect the colour;

concentrated sulphuric acid produces a blue solution. Wool is dyed red from an acid bath.

**Azo Cochineal** is prepared from diazotised *o*-anisidine and  $\alpha$ -naphthol-4:8-disulphonic acid, and consists of a red powder which is easily soluble in water and gives a dark red solution in concentrated sulphuric acid. The colour of the aqueous solution is not altered by hydrochloric acid or sodium hydroxide. Wool is dyed red from an acid bath.

**Sorbin Red** (*B.A.S.F.*) [*Azogrenadin S* (*By*) *Lanafuchsin SB* (*Cassella*)] is prepared from acetyl-*p*-phenylenediamine and  $\alpha$ -naphthol-3:6-disulphonic acid. It is a dark red powder which dissolves with a crimson red colour in water or alcohol. The aqueous solution is not changed by hydrochloric acid but with sodium hydroxide it turns brown. Concentrated sulphuric acid gives a dark crimson colour. **Lanafuchsin SG** has similar properties, but gives a yellower shade of red.

**Ponceau 6R** is prepared from  $\alpha$ -diazonaphthalene-4-sulphonic acid and  $\beta$ -naphthol-3:6:8-trisulphonic acid. The sodium salt is a brown powder which dissolves in water with a magenta-red colour, and gives a violet solution in concentrated sulphuric acid. The colour of the aqueous solution is unchanged by hydrochloric acid, whilst sodium hydroxide turns it brownish red. It dyes wool red from an acid bath.

**Chrome Brown P** (*Poirrier*) is prepared by the action of picramic acid on *m*-aminophenol.

**Acid Alizarin Black R** (*M. L. Br.*) is prepared from diazotised 6-nitro-2-aminophenol-4-sulphonic acid and  $\beta$ -naphthol. The solution in water is brownish violet, and is changed to red by hydrochloric acid or sodium hydroxide. It gives a reddish violet solution in concentrated sulphuric acid.

**Brilliant Sulphone Red B** (*Sandos*) is a red powder which dissolves in water with a bluish red colour. The solution is unchanged by hydrochloric acid or sodium hydroxide. Concentrated sulphuric acid produces a red solution which becomes bluish red on dilution. Wool is dyed bright red from a boiling bath.

**Fast Sulphone Violet 4R** (*Sandos*) is a violet-black powder which dissolves easily in water with a reddish violet colour. Hydrochloric acid and sodium hydroxide do not cause any change. Concentrated sulphuric acid dissolves the dye with a violet colour which becomes reddish violet on dilution.

**Fast Sulphone Violet 5BS** (*Sandos*<sup>1</sup>) is a greenish black powder which gives a violet solution in water. A brick-red precipitate is produced in the aqueous solution by hydrochloric acid; sodium hydroxide produces a brownish red colour. A red solution is obtained in con-

<sup>1</sup> B. P. 22886 of 1899.



centrated sulphuric acid, from which a brick-red precipitate is produced on dilution with water.

### 3. Azo Dyes from Carboxylic Acids.

All dyes belonging to this class possess a remarkable tendency to unite with metallic mordants, particularly with chromium compounds.

**Alizarin Yellow GG.**—The dye prepared by coupling diazotised *m*-nitroaniline and salicylic acid possesses, like the alizarin dyes, the property of being fixed by metallic mordants.

It is brought on the market as a paste and produces, especially when chromed, a yellow tinged with green which is very fast to light and soap.

It is employed in calico-printing as a substitute for Persian berries and as a substitute for fustic in wool dyeing.

**Alizarin Yellow R** is obtained from diazotised *p*-nitroaniline and salicylic acid. The commercial product is a paste containing 20 per cent. of the acid, which is insoluble in water. The sodium salt occurs in **Terracotta R** (*Geigy*), which is prepared by the nitration of benzene-azosalicylic acid; it is a brownish yellow powder, which is soluble in water and is turned red by sodium hydroxide; hydrochloric acid produces a brownish yellow precipitate whilst concentrated sulphuric acid gives an orange-yellow solution. Chromed wool is dyed yellowish brown.

**Persian Yellow** (*Geigy*) is obtained by the nitration of *p*-toluene-azosalicylic acid, and is put on the market as a brown, 20 per cent. paste, which gives a yellow solution in boiling water. The solution is coloured orange-brown by sodium hydroxide. Concentrated sulphuric acid gives an orange-yellow solution. Chromed wool is dyed yellow.

**Chrome Yellow GG** (*Akt. Ges.*) is prepared from diazotised *o*-anisidine and salicylic acid.

**Mordant Yellow**<sup>1</sup> (Anthracene Yellow BN, Milling Yellow) is prepared from  $\beta$ -diazonaphthalene-7- or 8-sulphonic acid and salicylic acid. It is a yellow powder which produces an orange-red solution in water; a dirty grey, gelatinous precipitate is produced in the aqueous solution by hydrochloric acid, and an orange-red precipitate by sodium hydroxide. Concentrated sulphuric acid gives an orange-red solution.

**Crumpsall Yellow** is prepared from diazotised  $\beta$ -naphthylamine-6:8-disulphonic acid and salicylic acid.

**Diamond Yellow G** (*Bayer*) is obtained by coupling *m*-diazobenzoic acid and salicylic acid, and occurs in the form of a greyish yellow paste, which is sparingly soluble in water, but dissolves easily in sodium carbonate or acetate, from which solutions hydrochloric acid produces a yellow precipitate. Concentrated sulphuric acid gives a reddish

<sup>1</sup> Nietzki, *Chemie der Organischen Farbstoffe*, 1906, p. 67.

yellow solution. The dye produces a yellow on chromed wool, which is very fast to light and milling.

The isomeric compound, obtained from *o*-aminobenzoic acid, is **Diamond Yellow R**, a brown paste which is very similar to the preceding substance in its reactions, but dyes wool a rather redder yellow.

**Anthracene Yellow C** (*Cassella*), obtained from tetrazotised thioaniline and 2 molecules of salicylic acid, is a brownish yellow powder which is sparingly soluble in water. Hydrochloric acid produces a dirty coloured precipitate in the greenish yellow solution; sodium hydroxide gives an orange-yellow solution, and sulphuric acid a dark brown solution. On diluting the latter with water a dirty brown precipitate is obtained.

**Anthracene Yellow GG**<sup>1</sup> (*Cassella*) dyes a purer and rather greener yellow than the C brand. The commercial product is a pale yellow powder which is sparingly soluble in cold water. The greenish yellow solution gives an orange-brown precipitate with hydrochloric acid; a large excess of sodium hydroxide also produces a precipitate. Concentrated sulphuric acid gives a yellow solution from which the dye is precipitated by dilution. It dissolves slightly in alcohol with a yellow colour.

**Anthracene Yellow R**<sup>2</sup> (*Cassella*) is a brownish yellow powder, which is sparingly soluble in cold water, but dissolves more easily in hot water, giving a brownish yellow solution. The dye separates out on cooling the hot solution. A brown precipitate is produced by hydrochloric acid, and an orange yellow precipitate by sodium hydroxide, in the aqueous solution. The solution in concentrated sulphuric acid is brownish violet; on dilution with water the dye is precipitated. The dye is slightly soluble in alcohol.

**Grenat en pâte** (*Sandoz*) is a brick-red, microcrystalline 10 per cent. paste which dissolves rather sparingly in water with a brick-red colour. With the aqueous solution, hydrochloric acid gives an eosin-red precipitate; sodium hydroxide produces a bluer red colour. Concentrated sulphuric acid gives a bluish red solution, from which, on dilution, an eosin-red precipitate is obtained.

In the presence of acids, it produces garnet-red shades directly on silk and wool; of more special value, however, are the bluer red lakes which are extremely fast to milling and light, and are obtained by boiling directly dyed cotton and wool with chromium fluoride. Consequently the dye is excellently adapted for admixture with alizarin dyes, logwood, and other dyes which yield chromium lakes.

**Eriochrome Phosphine R** (*Geigy*) is prepared from diazotised *p*-nitroaniline-*o*-sulphonic acid and salicylic acid. The yellowish orange

<sup>1</sup> *Rev. Mat. Gen. Col.*, 1898, 2, 420.

<sup>2</sup> *Ibid.*, 1898, 2, 420.

aqueous solution becomes pale orange with hydrochloric acid and blue-red with sodium hydroxide. It gives a yellowish orange solution with concentrated sulphuric acid.

**Alizarin Yellow 5G** (*M. L. Br.*) [Azoalizarin Yellow 6G (Durand, Huguenin), Tartrachromin GG (Bâle Co.)] is prepared from *p*-phenetidine and salicylic acid.

**Diamond Flavin C** is prepared by combining tetrazotised benzidine with one molecule of salicylic acid and boiling the product. It is a yellowish brown paste or powder which dissolves in water when sodium acetate is added. It gives a blood-red solution with concentrated sulphuric acid.

#### 4. Dihydroxynaphthaleneazo Dyes.

**Azofuchsin B** (*Bayer*), obtained from diazotoluene and 1:8-dihydroxy-naphthalene-4-sulphonic acid S, is a blackish brown powder which dissolves in water with a bluish red colour. Hydrochloric acid turns the solution red and produces a reddish brown precipitate; the solution becomes bluer with sodium hydroxide. Concentrated sulphuric acid gives a violet solution which becomes bluish red on dilution.

**Azofuchsin G** (*Bayer*) is prepared from *p*-diazobenzenesulphonic acid and 1:8-dihydroxynaphthalene-4-sulphonic acid S. It is a reddish brown powder, which dissolves in water with a bluish red colour; the solution is rendered yellower by hydrochloric acid and bluer by sodium hydroxide. Concentrated sulphuric acid gives a violet solution which becomes bluish red on dilution.

**Azo Acid Violet 4R** (*Bayer*) is a dark brown powder, and probably also belongs, like the three following dyes, to this class. The red aqueous solution becomes bluer on the addition of hydrochloric acid. Sodium hydroxide produces a soluble, orange-red precipitate. The solution in concentrated sulphuric acid is violet-red.

**Red G for Silk** (*B.A.S.F.*).<sup>1</sup> The commercial product is a red powder, which dissolves in water with an orange-red colour. The solution gelatinises by cooling. The alcoholic solution has an orange colour. Hydrochloric acid produces a gelatinous, brown precipitate in the aqueous solution. An excess of sodium hydroxide causes incomplete precipitation. The dye dissolves in concentrated sulphuric acid with a magenta-red colour; a dirty brown precipitate is produced by dilution. The boiling aqueous solution is decolorised by stannous chloride and hydrochloric acid.

Silk is dyed a bright red from an acid, boiled-off liquor bath.

**Red R for Silk** (*B.A.S.F.*).<sup>2</sup> Dyes silk a bluer red and a purer shade than roccellin. It is a reddish brown powder which is slightly soluble in cold water, but gives a cherry-red solution in hot water. Crystals

<sup>1</sup> *Rev. Gen. Mat. Col.*, 1898, 2, 386.

<sup>2</sup> *Ibid.*

separate from the hot solution by cooling. The alcoholic solution has a red colour. Hydrochloric acid produces a brown precipitate in the aqueous solution. Sodium hydroxide turns the solution darker and reddish violet. Concentrated sulphuric acid gives a violet-red solution, from which a brown precipitate separates on dilution with water.

The substance is decolorised by heating with stannous chloride and hydrochloric acid.

**Azo Acid Carmin B** (*M. L. Br.*)<sup>1</sup> is a brown powder which dissolves easily in water with a bluish red colour. The aqueous solution is unchanged by hydrochloric acid or sodium hydroxide. Concentrated sulphuric acid gives a yellowish brown solution, which becomes bluish red on dilution with water. It dyes wool from an acid bath like azo-fuchsin and equalises well.

**Roxamin** (*Durand, Huguenin, & Co.*) is obtained from diazo- $\alpha$ -naphthalene-4-sulphonic acid and 2:7-dihydroxynaphthalene. It is a brick-red powder giving a scarlet-red solution in water, which is unchanged by hydrochloric acid, but is darkened by sodium hydroxide. Concentrated sulphuric acid gives a deep violet solution. The dye is used as an archil-substitute.

**Chromazone Red A** (*Geigy*) is the sodium salt of benzaldehydeazo-1:8-dihydroxynaphthalene-3:6-disulphonic acid, and dyes wool in brilliant wine-red shades in an acid bath.

**Chromazone Blue R** (*Geigy*) is the sodium salt of the ethylphenyl-hydrazone of benzaldehydeazo-1:8-dihydroxynaphthalene-3:6-disulphonic acid. It gives blue colours on chromed wool which are very fast to milling and to acid.

**Chromotrope Dyes** (*M. L. Br.*) are produced by the combination of various diazo compounds with chromotropic acid (1:8-dihydroxynaphthalene-3:6-disulphonic acid), and can be used with or without mordants. In an acid bath wool is dyed in more or less bluish shades of red; on treatment with potassium bichromate these are changed to dark blue or black, as indicated in the following table:—

	Direct colour.	After treatment with Potassium Bichromate.
Chromotrope 2R	Cochineal scarlet	Navy blue.
" 2B	Bluish scarlet	Blackish blue.
" 6B	Magenta red •	Grey.
" 8B	Bluish magenta red	Greyish black.
" 10B	Violet	...
" FB	Crimson	Purple blue.

**Victoria Violet 4BS** is obtained by eliminating the acetyl group from chromotrope 6B or by the alkaline reduction of chromotrope 2B, and

<sup>1</sup> *Rev. Gen. Mat. Col.*, 1899, 3, 90.

is therefore the sodium salt of *p*-aminobenzeneazo-1:8-dihydroxynaphthalene-3:6-disulphonic acid. It is a grey-green powder which dissolves in water with a dark violet colour. The solution becomes yellowish red on the addition of hydrochloric acid or of sodium hydroxide. Concentrated sulphuric acid produces a bluish red solution, from which yellowish red flocks are precipitated on dilution with water.

Similar compounds occur in **Victoria Violet 8BS** and **Azo Acid Blue B**.

**Diamond Black PV** (*Bayer*) is prepared from *o*-aminophenol-sulphonic acid and 1:5-dihydroxynaphthalene. In comparison with other brands of diamond black (disazo dyes) it is weaker, but is probably the fastest black known.

### 5. Aminonaphtholazo Dyes.

**Lanacyl Dyes** (*Cassella*) are fast azo dyes, which are obtained from diazotised *peri*-aminonaphtholsulphonic acids and secondary  $\alpha$ -naphthylamines or 1:5-aminonaphthol. The shades produced on wool in an acid bath are fast to alkali, acid, and light.

**Lanacyl Violet B**, prepared from 1:8-aminonaphthol-3:6-disulphonic acid and ethyl- $\alpha$ -naphthylamine, is a blackish brown powder, which dissolves in water with a violet-red colour. The colour becomes redder with hydrochloric acid, and pale ponceau red with sodium hydroxide. The dye dissolves in concentrated sulphuric acid with a greenish blue colour.

**Lanacyl Blue R** dissolves in water with a reddish violet colour; it behaves similarly to the preceding.

**Lanacyl Blue BB** (Indigo Substitute) is obtained by coupling diazotised 1:8-aminonaphthol-3:6-disulphonic acid and 1:5-aminonaphthol. It dissolves in water with a violet colour; the colour becomes redder on treatment with hydrochloric acid or sodium hydroxide. Concentrated sulphuric acid produces a greenish blue solution.

**Lanacyl Navy Blue** dissolves in water with a bluish violet colour. The colour of the aqueous solution is not affected by hydrochloric acid, and is changed to reddish violet by sodium hydroxide. Concentrated sulphuric acid gives a green solution.

**Anthracene Chrome Black** (*Cassella*) is prepared from 3-amino- $\beta$ -naphthol-7-sulphonic acid R and  $\beta$ -naphthol.

**Palatine Chrome Blue** (*B.A.S.F.*), **Eriochrome Blue Black R** (*Geigy*), are diazotised 1-amino-2-naphthol-4-sulphonic acid combined with  $\beta$ -naphthol.

**Eriochrome Black A** (*Geigy*) is prepared from diazotised 8-nitro-1-amino- $\beta$ -naphthol-4-sulphonic acid and  $\beta$ -naphthol. The dark blue aqueous solution gives a reddish brown precipitate with hydrochloric

acid, and becomes cherry-red with sodium hydroxide. Concentrated sulphuric acid gives a dark violet-black solution.

**Eriochrome Red B** (*Geigy*) is prepared from diazotised 1-amino- $\beta$ -naphthol-4-sulphonic acid and phenylmethylpyrazolone. The yellowish red aqueous solution gives a scarlet-red precipitate with hydrochloric acid, and becomes orange-yellow with sodium hydroxide. Concentrated sulphuric acid gives a magenta-red solution.

**Chrome Fast Cyanin G** (*Basle Co.*) is prepared from diazotised 1-amino-2-naphtholsulphonic acid and  $\alpha$ -naphthol.

## 6. Disazo Dyes.

In consequence of the presence of an amino group, aminoazobenzene and its homologues can be converted, by treatment with nitrous acid, into diazo compounds which, like diazobenzene and its homologues, couple with amines and phenols to form dyes. These dyes contain, therefore, two azo groups, N:N. Of the greatest technical importance are those dyes which are prepared from  $\beta$ -naphthol and its sulphonic acids.

**Biebrich Scarlet** (New Red L, Imperial Scarlet, Ponceau B, etc.) is prepared from diazotised aminoazobenzenedisulphonic acid and  $\beta$ -naphthol. It is a reddish brown powder, which dissolves in water with a yellowish red colour. A dark red, flocculent precipitate is produced in the aqueous solution by hydrochloric acid, and brown flocks by sodium hydroxide. The calcium salt of the sulphonic acid is insoluble. Concentrated sulphuric acid gives a fine green solution the colour of which is changed through violet to red on dilution with water; finally a brown precipitate is produced. When a faintly alkaline solution of the dye is treated with zinc dust or sodium amalgam, the  $\beta$ -naphthol is eliminated as aminonaphthol, and aminoazobenzenedisulphonic acid is regenerated.

Wool and silk are dyed a beautiful, cochineal red from an acid bath.

**Crocein Scarlet 3B** (Ponceau 4RB) is the commercial name of an isomeric disulphonic acid which is obtained by coupling diazotised aminoazobenzenesulphonic acid and  $\beta$ -naphthol-8-sulphonic acid. The sodium salt is a scarlet-red, crystalline powder, which dissolves very easily in water with a fine red colour. On treatment with hydrochloric acid the solution deposits the acid (or probably an acid salt) in the form of almost black crystals with a green reflex. The dye dissolves in concentrated sulphuric acid with a blue colour, which is changed to red on dilution with water.

The dye is not precipitated from its solution by alum (difference from Biebrich scarlet). Barium chloride produces in the solution of the

sodium salt a precipitate which is changed on boiling into almost insoluble, black, crystalline leaflets. The dye produces a rather yellower shade of red than Biebrich scarlet, and is one of the finest red azo dyes.

**Eriochrome Verdone A** (*Geigy*). Sulphanilic acid is diazotised and combined with *m*-amino-*p*-cresol, and the product is diazotised and combined with  $\beta$ -naphthol. Concentrated sulphuric acid gives a green solution. Wool is dyed in claret-red shades from an acid bath, which on chroming become blue-green.

Numerous other dyes, such as the following, can be prepared by means of various  $\beta$ -naphtholsulphonic acids:—

Trade name.	From diazotised	Coupled with
Brilliant Croceïn . .	Aminoazobenzene	$\beta$ -Naphthol-6 : 8-disulphonic acid. $\beta$ -Naphthol-8-sulphonic acid B.
Croceïn Scarlet 7B . .	Aminoazotoluenesulphonic acid	
Croceïn Scarlet Oextra .	Aminoazobenzenedisulphonic acid	"
Fast Scarlet B . . .	Aminoazobenzenesulphonic acid	$\beta$ -Naphthol-6-sulphonic acid S.
Fast Ponceau 2B . . .	Aminoazobenzenedisulphonic acid	$\beta$ -Naphthol-3 : 6-disulphonic acid R.
Bordeaux G . . . .	Aminoazotoluenesulphonic acid	$\beta$ -Naphthol-6-sulphonic acid S.
Bordeaux BX . . . .	Aminoazoxylendisulphonic acid	$\beta$ -Naphthol.
Erythrin X . . . .	Aminoazobenzene	$\beta$ -Naphtholtrisulphonic acid.
Croceïn B . . . . .	"	$\alpha$ -Naphthol-4 : 8-disulphonic acid Sch.
Croceïn 3B . . . . .	Aminoazotoluene	$\alpha$ -Naphthol-4 : 8-disulphonic acid Sch.

**Cloth Reds.**—Many dyes are brought on the market under the name "Cloth Reds," and are employed for the dyeing of unmordanted wool or of chromed wool. For example:—

Trade name.	From diazotised	Coupled with
Cloth red G (Bayer) .	Aminoazobenzene	$\alpha$ -Naphthol-4-sulphonic acid NW.
" red B . . . . .	Aminoazotoluene	"
" red 3G " . . . .	"	$\beta$ -Naphthylamine-6-sulphonic acid Br.
" red 3B " . . . .	"	Ethyl- $\beta$ -naphthylamine-7-sulphonic acid.
" red G (Oehler) .	"	$\beta$ -Naphthol-6-sulphonic acid S.
" red B " . . . .	"	$\beta$ -Naphthol-3 : 6-disulphonic acid R.
[Fast milling " red B (Levinstein)]		
Cloth red G (Kalle) .	Aminoazobenzenesulphonic acid	$\beta$ -Naphthol.
" scarlet R . . . .	Aminoazotoluenesulphonic acid	"

**Milling Orange** (*Dahl*), obtained from diazoazobenzenesulphonic acid and salicylic acid, dyes chromed wool orange-red. It is a powder which is soluble in water. Hydrochloric acid and sodium hydroxide produce respectively a greyish yellow and a dark red precipitate; concentrated sulphuric acid gives a violet solution.

**Azo Blacks.**—Products are brought on the market under this name which are obtained by the action of diazotised aminonaphthalene-sulphonic acids (or aminonaphthaleneazobenzenesulphonic acids, etc.) on naphtholsulphonic acids, naphthylaminesulphonic acids, phenyl- $\alpha$ -naphthylamine, etc. They are employed extensively in wool dyeing. The aminoazosulphonic acids here considered are prepared by coupling diazotised aminosulphonic acids ( $\beta$ -naphthylamine-8-sulphonic acid,  $\beta$ -naphthylamine-6:8-disulphonic acid G, etc.) and  $\alpha$ -naphthylamine (or aminonaphthyl ethers). Such products are derivatives, therefore, of aminoazonaphthalene and its analogues; they are disazo dyes containing naphthylamine in the “middle” position.

Such dyes are :—

Trade name.	From diazotised	Coupled with	The product is diazotised and coupled with
Naphthol black B (Cassella)	$\beta$ -Naphthylamine-3:6-disulphonic acid G	$\alpha$ -Naphthylamine	$\beta$ -Naphtholdisulphonic acid R.
Naphthol black 6B (Cassella)	$\alpha$ -Naphthylaminedisulphonic acid	„	$\beta$ -Naphtholdisulphonic acid R.
Azo black O (M. L. Br)	$\beta$ -Naphthylaminemono- (or di-) sulphonic acid	„	$\beta$ -Naphtholdisulphonic acid R.
Naphthylamine black D (Cassella)	$\alpha$ -Naphthylaminedisulphonic acid	„	$\alpha$ -Naphthylamine.
Blue black B (B.A.S.F.)	$\beta$ -Naphthylamine-8-sulphonic acid	„	$\beta$ -Naphtholdisulphonic acid R.
Jet black (Bayer)	Aminobenzenedisulphonic acid	„	Phenyl- $\alpha$ -naphthylamine.
Diamond black (Bayer)	Aminosalicylic acid	„	$\alpha$ -Naphthol-4-sulphonic acid NW.
Victoria black B (Bayer)	Sulphanilic acid	„	Dihydroxynaphthalenesulphonic acid S.
Anthracite black B (Cassella)	$\alpha$ -Naphthylamine-3:6-disulphonic acid	„	Diphenyl- <i>m</i> -phenylenediamine.
Sulphoncyanines	Metanilic acid	„	Phenyl- and tolyl-1-naphthylamine-8-sulphonic acids.
Biebrich patent black BO (Kalle)	$\alpha$ -Naphthylaminedisulphonic acid	$\alpha$ -naphthylamine sulphonic acids (1:6 and 1:7)	$\beta$ -Naphtholdisulphonic acid R.
Biebrich patent black 4AN (Kalle)	Naphthionic acid	„	$\alpha$ -Naphthylamine.
Anthracene acid black (Cassella)	Aminosalicylic acid	„	$\beta$ -Naphtholdisulphonic acid R.
Naphthalene acid black (Bayer)	Metanilic acid	„	$\alpha$ -Naphthylamine
Wool black	Aminoazobenzenesulphonic acid	$\beta$ -Tolyl- $\beta$ -naphthylamine	...

Probably this class should also include the following dyes, the compositions of which must be very nearly allied to the preceding.



**Patent Black (B.A.S.F.)** is an acid dye, recommended as a substitute for logwood.

**Chrome Patent Blacks TG, TB, T, TR (Kalle)** are wool dyes, which are employed in an acid bath, the fabric being subsequently treated with 1.5 per cent. potassium bichromate.

**Diaminogen Black (Cassella)** is prepared from diazotised acetyl-1:4-naphthylenediamine-7-sulphonic acid and  $\alpha$ -naphthylamine, the product being diazotised, coupled with 8-amino- $\beta$ -naphthol-6-sulphonic acid G, and subsequently hydrolysed.

**Diaminogen Blue BB (Substitute for Indigo)** is prepared like the preceding dye, but contains  $\beta$ -naphthol-6-sulphonic acid instead of aminonaphtholsulphonic acid G.

**Diaminogen Blue G** contains  $\beta$ -naphthol-3:6-disulphonic acid as the final component.

**Azo Acid Black TL extra (M. L. Br.)**<sup>1</sup> is a reddish brown powder which dissolves in water with a blackish violet colour. Hydrochloric acid produces an orange-red precipitate in the aqueous solution. Sodium hydroxide changes the colour of the solution to brownish violet. Stannous chloride and hydrochloric acid reduce it. The dye dissolves in concentrated sulphuric acid with a yellowish red colour which becomes yellowish brown on dilution with water. The dye is sparingly soluble in alcohol.

It consists of a mixture of a blackish blue, a green, a violet-blue, and an orange dye. Wool is dyed black from an acid bath containing sodium sulphate.

**Wool Black N4B (Bayer)**<sup>2</sup> is a black powder which dissolves in cold water with a blackish violet colour, and consists of a mixture of a reddish black and a greenish blue dye. The solution deposits a bluish black precipitate on adding hydrochloric acid, and is turned blue by sodium hydroxide. The dye gives a greenish black solution in concentrated sulphuric acid, from which a blackish blue precipitate is produced on the addition of water. From a bath containing sodium sulphate and acetic acid wool is dyed in bluish black shades similar to those obtained with logwood. The colours can be discharged by stannous chloride and by zinc dust.

**Nerol Blacks B and BB (Akt. Ges.)**<sup>3</sup> prepared from *p*-aminodiphenylaminesulphonic acid,  $\alpha$ -naphthylamine (in middle position) and  $\alpha$ -naphthol-4-sulphonic acid and  $\beta$ -naphthol-3:6-disulphonic acid respectively, are blackish blue powders, which dissolve in warm water with a violet-black (B) or a bluish violet-black colour. Hydrochloric acid produces in the solutions a bluish black precipitate, and sodium hydroxide a violet-black precipitate. Greenish blue solutions

<sup>1</sup> *Rev. Gen. Mat. Col.*, 1899, 3, 198.

<sup>2</sup> *Ibid.*, 1899, 3, 125.

<sup>3</sup> *Ibid.*, 1899, 3, 319.

are formed in concentrated sulphuric acid, which become reddish blue on dilution with water and finally blackish blue.

Both brands contain an admixture of a reddish brown dye. They are used for dyeing wool, and are applied in the presence of sodium sulphate and acetic acid. The colours are very fast to washing.

**Wool Black** (*Man. néer. Delft*)<sup>1</sup> is a dye analogous to naphthol black, and contains H-acid as the third component. It dyes wool best from a bath containing acetic acid.

It is a violet-black powder which dissolves very easily in cold water with a blackish violet colour. Hydrochloric acid and sodium hydroxide produce violet-black precipitates in the aqueous solutions. Concentrated sulphuric acid gives a greenish black solution.

**Union Blacks B and R** (*Bayer*)<sup>2</sup> are brownish black powders which dissolve in water with bluish black colours. Sodium hydroxide produces a blackish blue, and hydrochloric acid a bluish black or blackish violet precipitate. The dyes give blue solutions in concentrated sulphuric acid.

Union goods are dyed suitably in a neutral bath containing sodium sulphate. The brand B gives a deep black; brand R a reddish black.

**Diamond Black 2B** (*Bayer*)<sup>3</sup> appears to be a mixture of a violet-black and a bluish green dye. It is a black powder which dissolves easily in water with a dark blue colour. The aqueous solution is unchanged by sodium hydroxide, whilst hydrochloric acid produces a dark blue precipitate. The dye dissolves in concentrated sulphuric acid with a greenish blue-black colour; on dilution a bluish black precipitate is formed.

Wool is dyed bluish black in the presence of sodium sulphate, acetic acid, and a little potassium bichromate.

**Dianil Black HW** (*M. L. Br.*)<sup>4</sup> is specially intended for the dyeing of mixed fabrics. Half-wool is dyed by a short immersion in a bath at 90—100° containing 20 to 30 per cent. of sodium sulphate; half-silk is dyed in a bath containing soap, sodium carbonate, and sodium chloride.

The dye is a bluish grey powder which dissolves in cold water with a bluish black colour. The solution is turned blackish violet by sodium hydroxide; hydrochloric acid produces a blackish blue precipitate. Concentrated sulphuric acid produces a greenish black solution which becomes blue on dilution with water and finally deposits a blackish blue precipitate.

<sup>1</sup> *Rev. Gen. Mat. Col.*, 1900, 4, 9.

<sup>2</sup> *Ibid.*, 1899, 3, 248.

<sup>3</sup> *Ibid.*, 1900, 4, 129.

<sup>4</sup> *Ibid.*, 1900, 4, 94.

**Copper Blue B** (*M. L. Br.*)<sup>1</sup> dyes wool in reddish blue shades in the presence of copper sulphate, according to a special process.

It is a brown powder which dissolves in water with a violet-blue colour. The colour of the solution is changed to yellowish red by hydrochloric acid; sodium hydroxide produces a bluish red precipitate. The violet solution in concentrated sulphuric acid remains violet at first after the addition of water, then becomes yellowish red, and finally bluish red.

**Copper Black S** (*M. L. Br.*)<sup>2</sup> is copper blue B shaded with a yellow dye.

**Tolylene Black G**, **Union Blacks B and T** (*Oehler*), **Palatine Black 4B** (*B.A.S.F.*), **Wool Black 6B** (*Akt. Ges.*)<sup>3</sup> are prepared by first coupling diazotised  $\alpha$ -naphthylamine with 1-amino-8-naphthol-4-sulphonic acid in alkaline solution and then combining diazotised sulphanilic acid with the product in acid solution.

The **Janus** dyes (*M. L. Br.*) constitute a group of strongly basic azo dyes which are characterised by a pronounced affinity for either animal or vegetable fabrics; on this account they are eminently adapted for dyeing half-woollen yarns and tissues in one bath, best in the presence of sodium sulphate and sulphuric acid. They can also be fixed on vegetable fabrics by means of tannin and antimony in the form of lakes which are very fast to soap and to boiling. Moreover they can be dyed on unmordanted cotton, and subsequently be converted into the fast tannin-antimony lakes by treatment in a bath containing tannin, antimony salt, and acid.

The yellow, red, and brown dyes are produced from diazo derivatives of aminophenylammonium and aminobenzylamine compounds, whilst the blue and the green dyes are azo derivatives of various safranines (related to indoine, see p. 1032). They are brought on the market under the following names:—

Janus Yellow R; Janus Brown R (*m*-aminophenyltrimethylammonium + *m*-toluidine + chrysoidine) and B; Janus Red B (*m*-aminophenyltrimethylammonium + *m*-toluidine +  $\beta$ -naphthol); Janus Bordeaux B; Janus Grey B (from diazosafranine and phenol) is identical with Diazine Black [Kalle]; Janus Blue R (from diazosafranine and  $\beta$ -naphthol) and G; Janus Dark Blue B and R; Janus Green B and G (from diazosafranine and dimethylaniline) is identical with Diazine Green [Kalle].

## 7. Tetrazo Dyes from Benzidine and its Analogues.

In the course of the last twenty-five years numerous azo dyes, possessing the property of dyeing unmordanted cotton, have been

<sup>1</sup> *Rev. Gen. Mat. Col.*, 1900, 4, 94.

<sup>2</sup> *Ibid.*, 1900, 4, 94.

<sup>3</sup> Jakobi, *Chem. Zeit.*, 1900, 24, 493.

prepared from benzidine and homologues or analogous bases. The colours are mostly very fast to soap; many are not so fast to light, whilst others are considerably changed by acids.

**Chrysamin G** is obtained by coupling tetrazodiphenyl with salicylic acid (2 mol.) and occurs as a yellowish brown powder or as a paste. It is very sparingly soluble in water. Hydrochloric acid produces a brown precipitate in the aqueous solution, whilst sodium hydroxide develops a reddish brown coloration. The reddish violet solution in sulphuric acid gives a brown precipitate on dilution with water.

Cotton is dyed yellow in the presence of 10 per cent. sodium phosphate and 2.5 per cent. soap solutions.

**Chrysophenin** is prepared by ethylating Brilliant Yellow. It is an orange-yellow powder which is sparingly soluble in cold water, but dissolves easily in hot water with a reddish yellow colour. A brown precipitate is produced in the aqueous solution by hydrochloric acid. Sodium hydroxide changes the colour of the solution to yellow and precipitates orange flocks. Concentrated sulphuric acid gives a reddish violet solution, from which a blue flocculent precipitate is obtained on dilution with water.

Cotton is dyed in a bath of sodium chloride or soap. Wool can be dyed in an alkaline or an acid bath.

**Pyramine Orange 3G (B.A.S.F.)**,<sup>1</sup> prepared from 1 mol. of benzidine and 1 mol. each of nitro-*m*-phenylenediamine and *m*-phenylenediamine-disulphonic acid, is an orange-brown powder which is sparingly soluble in cold water, but dissolves in warm water with an orange-yellow colour. The solution gives an orange-yellow precipitate with sodium hydroxide and a brown precipitate with hydrochloric acid. Concentrated sulphuric acid produces a brownish yellow solution, from which on the addition of water a bluish red precipitate, finally becoming yellowish brown, is obtained.

The dye is applied in the presence of sodium sulphate and sodium carbonate, and is used specially for dyeing cotton, but can also be used for wool, silk, half-wool, and half-silk. The colours are yellower than those produced by other brands of pyramine orange.

Other products, which directly dye cotton yellow or brown, are:—

Diamine Yellow A; Diamine Fast Yellow B; (prepared by the action of hypochlorites on sodium dehydrothiotoluidinesulphonate or on the latter together with primuline) Diamine Orange G and B; Cotton Brown A, N, 3G; Diazo Brown; and those given in the following table:—

<sup>1</sup> *Rev. Gen. Mat. Col.*, 1899, 3, 250.

Trade name.	Produced by diazotising	And coupling with
Chrysamin R .	Tolidine	2 mol. salicylic acid.
Cresotin yellow G .	Benzidine	2 " cresotic acid.
" yellow R .	Tolidine	2 " "
Diamine yellow N .	Ethoxybenzidine	1 " salicylic acid } Ethylated 1 " phenol } after coupling.
Benzo orange .	Benzidine	1 " salicylic acid.
Tolylene orange G .	Tolidine	1 " naphthionic acid.
" orange R .	"	1 " cresotic acid.
" orange RR .	<i>m</i> -Tolylenediaminesulphonic acid	1 " <i>m</i> -tolylenediaminesulphonic acid.
Columbia yellow } Tolylene yellow }	<i>m</i> -Tolylenediaminesulphonic acid	2 " $\beta$ -naphthylamine. "
Pyramine orange R .	Benzidinedisulphonic acid	2 " nitro- <i>m</i> -phenylenediamine.
Alkali yellow R .	Benzidine	2 " salicylic acid. "
Carbazole yellow .	Diaminocarbazole	1 " dehydrothio- <i>p</i> -toluidinesulphonic acid.
Brilliant yellow .	Diaminostilbenedisulphonic acid	2 " salicylic acid.
Hessian yellow .	Diaminostilbenedisulphonic acid	2 " phenol.
Diamine gold .	1 : 5-Naphthylenediamine-3 : 7-disulphonic acid	2 " salicylic acid.
Cotton yellow G .	<i>p</i> -Aminoacetanilide	2 " phenol (ethylated after coupling).
Cloth orange .	Benzidine	Salicylic acid (hydrolysed after coupling and then treated with phosgene.)
" brown R .	"	1 mol. salicylic acid.
" brown G .	"	1 " resorcinol.
Diamine brown V .	"	1 " salicylic acid.
" brown M .	"	1 " $\alpha$ -naphtholsulphonic acid NW.
" brown B .	"	1 " salicylic acid.
		1 " 2 : 7-dihydroxynaphthalene.
		1 " aminonaphtholsulphonic acid G (alkaline).
		1 " <i>m</i> -phenylenediamine.
		1 " salicylic acid.
		1 " aminonaphtholsulphonic acid G.
		1 " salicylic acid.
		1 " phenylaminonaphtholsulphonic acid G.

**Congo Red** is produced from 1 mol. of benzidine and 2 mol. of naphthionic acid. The free sulphonic acid has a brown colour, whilst its salts are red. The commercial product is a reddish brown powder which dissolves in water with a reddish brown colour. The solution gives a blue precipitate with hydrochloric acid, and a bluish violet precipitate with dilute acetic acid. Sodium hydroxide produces a red precipitate which is soluble in water. Concentrated sulphuric acid produces a blue solution. Cotton is dyed red in a bath containing soap and sodium chloride or sulphate. The red colour is changed to blue even by dilute acids. This blue is extremely sensitive to alkalis, prolonged washing, even with water, being sufficient to restore the red colour. The blue colour is also changed to red by aniline (application of Congo Red in the titration of aniline, p. 853).

**Benzopurpurine 4B** is obtained from 1 mol. of tolidine and 2 mol. of naphthionic acid. It resembles Congo red, but is less sensitive to acids. It is a brown powder which dissolves in water with a brownish red colour. In other respects it behaves like the preceding dye.

**Deltapurpurine 5B** is prepared from 1 mol. of tolidine and 1 mol. each of  $\beta$ -naphthylamine-6-sulphonic acid, and  $\beta$ -naphthylamine-7-sulphonic acid. It is also less sensitive than Congo red to acids.

**Diamine Red 10B** (*Cassella*)<sup>1</sup> dyes cotton crimson-red in the presence of 2 per cent. sodium carbonate and 20 per cent. sodium sulphate. It is coloured blackish blue by concentrated sulphuric acid, olive-green by hydrochloric acid, and is not changed by sodium hydroxide.

**Anthracene Red** is obtained by coupling *o*-nitrotetrazodiphenyl with 1 mol. each of salicylic acid and  $\alpha$ -naphthol-4-sulphonic acid NW. The commercial product is a brownish red powder which is sparingly soluble in cold water, but dissolves more readily in hot water with a red colour. The aqueous solution is unchanged by sodium hydroxide, and gives a red flocculent precipitate with hydrochloric acid. The crimson-red solution in concentrated sulphuric acid deposits a brownish red precipitate on dilution with water. It is not suitable for dyeing cotton, but gives good results on unmordanted or chromed wool.

**Salicin Reds 2G, G, and B** (*Kalle*).<sup>2</sup>—The first is a brown, the second a reddish brown, and the last a greenish black, powder. They dissolve even in cold water with yellowish red or bluish red colours. Hydrochloric acid produces in a concentrated solution a reddish brown precipitate which is redissolved on the addition of a large quantity of water.

The three dyes, in the order given, produce yellowish brown, yellowish red, and bluish red solutions respectively in sodium hydroxide. Concentrated sulphuric acid produces cherry-red, or violet (B) solutions.

They give yellowish red to bluish red shades on wool in the presence of 10 per cent. sodium sulphate and 2 per cent. sulphuric acid. By subsequent treatment with 1 per cent. potassium bichromate or 1 per cent. chromium fluoride (in the same bath), colours are obtained which are not so bright but are fast to milling. The brand B is prepared from nitrobenzidine and 1 mol. each of salicylic acid and  $\beta$ -naphthol, the product being subsequently sulphonated.<sup>3</sup>

**Rosophenin 4B** (*Clayton Aniline Co.*), **St Denis Red** (*Poirrier*), **Dianthin** (*Claus & Co.*), are prepared from diaminoazoxytoluene and 2 mol. of  $\alpha$ -naphtholsulphonic acid NW. The commercial product is a red powder which is slightly soluble in alcohol and dissolves in water

<sup>1</sup> *J. Soc. Dyers and Col.*, 1899, 15, Pattern sheet No. 43.

<sup>2</sup> *Rev. Gen. Mat. Col.*, 1899, 3, 250.

<sup>3</sup> *Chem. Zeit.*, 1900, 24, 493.

with a red colour. The aqueous solution gives a red precipitate with hydrochloric acid, and a brick-red precipitate with sodium hydroxide. Concentrated sulphuric acid produces a red solution, from which the dye is obtained as a red precipitate on dilution with water. It dyes cotton less readily than do the benzidine dyes, and is applied in a bath containing sodium hydroxide.

Trade name.	Produced by diazotising	And coupling with
Diamine fast red F: Azidine fast red F	Benzidine	1 mol. salicylic acid.
Diamine scarlet B	"	1 " aminonaphtholsulphonic acid G.-phenol.
		1 " $\beta$ -naphtholdisulphonic acid G (ethylated after coupling).
Benzopurpurine B	Tolidine	2 " $\beta$ -naphthylamine-6-sulphonic acid (Brönner).
Benzopurpurine 6B	"	2 " $\alpha$ -naphthylamine-5-sulphonic acid L.
Diamine red B	"	1 " $\beta$ -naphthylamine-7-sulphonic acid F.
		1 " $\beta$ -naphthylamine-6-sulphonic acid Br.
Diamine red 3R	"	2 " $\beta$ -naphthylamine-7-sulphonic acid F.
Rosazurine G	"	1 " ethyl- $\beta$ -naphthylamine-7-sulphonic acid F.
		1 " $\beta$ -naphthylamine-7-sulphonic acid F.
Rosazurine B	"	2 " ethyl- $\beta$ -naphthylamine-7-sulphonic acid F.
Brilliant purpurine R	"	1 " $\beta$ -naphthylamine-3:6-disulphonic acid R.
		1 " naphthionic acid.
Congo 4R	"	1 " "
		1 " resorcinol.
Brilliant Congo R	"	1 " $\beta$ -naphthylamine-3:6-disulphonic acid R.
		1 " $\beta$ -naphthylamine-6-sulphonic acid Br.
Glycine red	Benzidine	1 " $\alpha$ -naphthylglycine.
		1 " naphthionic acid.
Brilliant Congo G	"	1 " $\beta$ -naphthylamine-3:6-disulphonic acid R.
		1 " $\beta$ -naphthylamine-6-sulphonic acid Br.
Hessian Bordeaux	Diaminostilbene-disulphonic acid	2 " $\alpha$ -naphthylamine.
Hessian purple N	"	2 " $\beta$ -naphthylamine.
Hessian brilliant purple	"	2 " $\beta$ -naphthylamine-6-sulphonic acid Br.
Hessian purple B	"	2 " mixture of $\beta$ -naphthylamine-6-sulphonic acid Br and $\beta$ -naphthylamine-7-sulphonic acid F.
Hessian purple D	"	2 " $\beta$ -naphthylamine-5-sulphonic acid D.
Salmon red (B.A.S.F.)	<i>p</i> -Aminoacetanilide	Naphthionic acid (hydrolysed after coupling, and then treated with phosgene).
Tolylenered (Oehler), Dianol brilliant red, (Levinstein), Chlorantine red (Soc. Chem. Ind. Basle)	Dichlorobenzidine	2 mol. $\beta$ -naphthylamine-3:6-disulphonic acid.

Diamine Bordeaux B and S belong to the same group, and

probably also **Benzo Red SG** (*Bayer*),<sup>1</sup> which is a brownish black powder, soluble even in cold water, with a bluish red colour.

The aqueous solution gives violet-red precipitates with sodium hydroxide and with hydrochloric acid. Concentrated sulphuric acid produces a violet-black solution, from which the dye is precipitated on dilution in violet-brown flocks. It dyes cotton directly in bluish red shades (similar to the Geranin colours), best in the presence of sodium sulphate and soap.

**Brown DSP** (*Poirrier*) is related to rosophenin 4B. It dissolves in strongly alkaline, boiling water, and dyes cotton in the presence of 20 per cent. sodium carbonate and 20 per cent. sodium chloride.

**Congo Corinth B** is obtained by coupling tetrazoditolyl with 1 mol. each of naphthionic acid and  $\alpha$ -naphtholsulphonic acid NW.

The commercial product is a greenish black powder which dissolves in water with a magenta-red colour. The aqueous solution gives a violet precipitate with hydrochloric acid, and a cherry-red coloration with sodium hydroxide. The blue solution in concentrated sulphuric acid yields a violet precipitate on dilution with water.

Cotton is dyed brownish violet.

**Benzoazurin G** results by the combination of diazotised dianisidine with 2 mol. of  $\alpha$ -naphtholsulphonic acid NW. The commercial product is a bluish black powder which dissolves in water with a bluish violet colour. The aqueous solution gives a violet precipitate with hydrochloric acid, and a red coloration with sodium hydroxide. A blue solution is produced in concentrated sulphuric acid, from which a precipitate is obtained on dilution with water. Cotton is dyed blue. The colour becomes reddish on warming and blue again on cooling.

**Diamine Blue 3R** is produced from ethoxybenzidine and 2 mol. of naphtholsulphonic acid NW. The commercial product is a black powder which dissolves easily in hot water, but is sparingly soluble in alcohol. The aqueous solution is unchanged by hydrochloric acid, but is coloured reddish violet by sodium hydroxide. Concentrated sulphuric acid produces a dark blue solution, from which a violet precipitate is obtained on dilution with water. Unmordanted cotton is dyed reddish blue.

**Diamine Sky Blue, Chlorazol Blue 6G** (*Holliday*) (Benzo Sky Blue) is obtained by coupling diazotised dianisidine with 2 mol. of aminonaphtholdisulphonic acid H in alkaline solution. It is a bluish black powder, which is insoluble in alcohol, and dissolves in water with a blue colour. The aqueous solution is darkened and becomes redder by treatment with sodium hydroxide. Hydrochloric acid is without action. Concentrated sulphuric acid dissolves the dye with a bluish green colour. Unmordanted cotton is dyed sky blue.

<sup>1</sup> *Rev. Gen. Mat. Col.*, 1900, 4, 129.



Analogous dyes are Diamine Blue RW, BG; Diamine New Blue R and G; the Chicago Blues; Chicago Grey; Diazo Blue; and Columbia Blue G and R.

Also the following:—

**Trisulphone Violet B** (*Sandoz*) is prepared from diazotised benzidine and 1 mol. of  $\alpha$ -naphtholtrisulphonic acid and 1 mol. of  $\beta$ -naphthol. It is a dark powder with a bronze lustre, which dissolves easily in water with a violet colour. The solution gives a bluish violet precipitate with hydrochloric acid, and a violet-red coloration with sodium hydroxide. Concentrated sulphuric acid produces a greenish blue solution, which yields a violet precipitate on dilution.

Unmordanted cotton is dyed a beautiful, clear violet in a neutral or faintly alkaline bath containing 30 per cent. sodium chloride; the bath is only partly exhausted. Much deeper colours are produced, however, by the addition of 2 per cent. alum.

From an acetic acid bath, wool is dyed in shades rather redder than those produced on cotton; also in the case of half-wool materials in a neutral bath, the wool is dyed more intensely and redder than the cotton.

**Trisulphone Blue R** (*Sandoz*) is prepared as the preceding dye, but using tolidine instead of benzidine. It is a dark powder with a bronze lustre, which dissolves easily in water with a bluish violet colour. The solution is turned reddish violet by sodium hydroxide. The greenish blue solution in concentrated sulphuric acid gives a violet precipitate on dilution. The dye is employed like trisulphone violet B, and dyes unmordanted cotton a fine reddish blue with a brownish shade. In mixed fabrics in a neutral bath the wool or the silk is dyed redder and more intensely than the cotton, just as is the case with trisulphone violet B.

**Trisulphone Blue B**, prepared as above, but with dianisidine, is a bluish grey powder, which dissolves easily in water with a sky-blue colour. The aqueous solution gives a blue precipitate with hydrochloric acid. Sodium hydroxide develops a reddish violet colour. Concentrated sulphuric acid produces a greenish blue solution, which gives a bluish violet precipitate on dilution.

The process of dyeing resembles that of trisulphone violet B; a bright blue is produced, the shade of which is intermediate between those of diamine blue 2B and 3B. Trisulphone blue B is very well adapted for dyeing mixed fabrics, since from a neutral or faintly alkaline bath, half wool and half silk are dyed nearly uniformly (the animal fibres are dyed a trifle stronger and redder).

The dye, like trisulphone blue R and trisulphone violet B, is affected by copper, which greatly reddens the shade. Treatment with 1 to 2 per cent. potassium bichromate in a cold bath scarcely affects the

shade of the three dyes and renders the colours distinctly faster to light and to washing.

**Diamine Black RO** (*Cassella*) is obtained by coupling 1 mol. of tetrazodiphenyl with 2 mol. of aminonaphtholsulphonic acid G in alkaline solution. The commercial product is a black powder which dissolves in water with a violet-black colour, but is sparingly soluble in alcohol. The aqueous solution develops a violet coloration with sodium hydroxide and gives a blue precipitate with hydrochloric acid. Concentrated sulphuric acid produces a blue solution which gives a reddish blue precipitate on dilution with water.

Unmordanted cotton is dyed a greyish blue. After diazotising and developing with suitable developers, such as  $\beta$ -naphthol or resorcinol, a deep black is produced.

**Diamine Black BH** is obtained from 1 mol. of benzidine and 1 mol. each of aminonaphtholsulphonic acid G and aminonaphtholdisulphonic acid H.

Trade name.	Produced by diazotising	And coupling with
Azo violet . . .	Dianisidine	1 mol. naphthionic acid.
Rosazurine B . . .	Tolidine	1 " $\alpha$ -naphtholsulphonic acid NW.
Congo Corinth G . . .	Benzidine	2 " ethyl- $\beta$ -naphthylamine-8-sulphonic acid.
Heliotrope 2B . . .	"	1 " naphthionic acid.
Benzo violet . . .	"	1 " $\alpha$ -naphtholsulphonic acid NW.
Diamine violet N . . .	"	1 " $\beta$ -naphthol-8-sulphonic acid B.
Oxamine violet . . .	"	1 " $\alpha$ -naphthol-4 : 8-disulphonic acid Sch.
Hessian violet . . .	Diaminostilbenedisulphonic acid	1 " $\alpha$ -naphtholsulphonic acid NW.
Diamine blue BB . . .	Benzidine	1 " $\alpha$ -naphthol-3 : 6-disulphonic acid.
Azo blue . . .	Tolidine	2 " aminonaphtholsulphonic acid G (in acid solution).
Diamine blue BX . . .	"	2 " 2-amino-5-naphthol-7-sulphonic acid (in alkaline solution).
Diamine blue 3B . . .	"	1 " $\alpha$ -naphthylamine.
Oxamine blue 3R . . .	"	1 " $\beta$ -naphthol.
Benzoazurin 3G . . .	Dianisidine	2 " aminonaphtholdisulphonic acid H (in alkaline solution).
Brilliant azurin 5G . . .	"	2 " $\alpha$ -naphtholsulphonic acid NW.
Direct blue B . . .	"	1 " " "
Diamine blue B . . .	Ethoxybenzidine	1 " aminonaphtholdisulphonic acid H (in alkaline solution).
		2 " aminonaphtholdisulphonic acid H (in alkaline solution).
		1 " $\alpha$ -naphtholsulphonic acid NW.
		1 " 2-amino-5-naphthol-7-sulphonic acid (in alkaline solution).
		2 " $\alpha$ -naphthol-5-sulphonic acid.
		2 " dihydroxynaphthalenesulphonic acid S.
		1 " $\alpha$ -naphtholsulphonic acid NW.
		1 " dihydroxynaphthalenesulphonic acid.
		1 " $\beta$ -naphthol-3 : 7-disulphonic acid $\delta$ .
		1 " $\alpha$ -naphtholsulphonic acid NW.

[Continued on next page]

Trade name.	Produced by diazotising	And coupling with
Naphthyl blue 2B.	Benzidinedicarboxylic acid	2 mol. Benzoyl-1-amino-8-naphthol-5-sulphonic acid.
Direct grey R	Benzidine	2 „ dihydroxynaphthalenesulphonic acid.
Azo black blue	Tolidine	1 „ <i>m</i> -hydroxydiphenylamine.
Azo mauve B	„	1 „ aminonaphtholdisulphonic acid H.
	„	1 „ $\alpha$ -naphthylamine.
	„	1 „ aminonaphtholdisulphonic acid H (in alkaline solution).
Direct blue R	„	1 „ $\alpha$ -naphtholsulphonic acid NW.
	„	1 „ dihydroxynaphthalenesulphonic acid.
Azidine wool blue R (C. Jäger)	„	1 „ $\beta$ -naphthol-8-sulphonic acid.
Direct grey B	„	1 „ 8-amino- $\alpha$ -naphthol-5-sulphonic acid.
	„	2 „ dihydroxynaphthalenesulphonic acid.
Diamine blue black E	Ethoxybenzidine	1 „ $\beta$ -naphthol-3 : 7-disulphonic acid $\delta$ .
	„	1 „ aminonaphtholsulphonic acid G (in alkaline solution).
Diamine black BO	„	2 „ aminonaphtholsulphonic acid G (in alkaline solution).
Violet black	<i>p</i> -Aminoacetanilide	1 „ $\alpha$ -naphtholsulphonic acid NW (the acetyl group eliminated, the intermediate product diazotised, and coupled with 1 mol. $\alpha$ -naphthylamine).
Nyanza black B	„	1 „ $\alpha$ -naphthylamine (saponification of the acetyl group, diazotisation of the intermediate product, and combination with 1 mol. of aminonaphtholsulphonic acid G).
Diazo black B	Benzidine	2 „ $\alpha$ -naphthylamine-5-sulphonic acid L.
„ brilliant black B	Tolidine	2 „ „ „
Diazurine	Dianisidine	2 „ „ „
Diamine sky blue FF	„	2 „ 1 : 8-aminonaphthol-2 : 4-disulphonic acid.
Chicago blue 6B, brilliant benzo blue 6B, diamine brilliant blue G, chlorazol sky blue FF	„	2 „ 1 : 8-chloronaphthol-3 : 6-disulphonic acid.
Chlorazol blue (Holiday)	„	2 „ chloro- $\alpha$ -naphthol-4 (or 5)-sulphonic acid.
Diamine deep black	Di- <i>p</i> -aminodiphenylamine	1 „ aminonaphtholsulphonic acid G and 1 mol. <i>m</i> -tolylene-diamine.

With the foregoing are to be included Diamine Black Blue B; Oxydiamine Deep Black N, NR, SOOO; Diazo Blue Black RS; Direct Deep Black R, T; Direct Blue Black B; Pluto Black (Bayer); Tabora Black; Zambesi Black BR.

**Zambesi Indigo Blue R** (*Akt. Ges.*)<sup>1</sup> is a dark violet powder which dissolves in water with a violet-black colour. The aqueous solution gives a blue precipitate with hydrochloric acid, and a blackish violet precipitate with sodium hydroxide. Concentrated sulphuric acid produces a greenish blue solution from which a blue precipitate of the dye is obtained on dilution with water.

<sup>1</sup> *Rev. Gen. Mat. Col.*, 1900, 4, 64.

It dyes cotton directly, and when diazotised on the fibre and developed with  $\beta$ -naphthol gives a rather reddish deep blue colour which is fast to washing, acid, and alkali.

**Rosanthrens O, R, A, B, CB** (*Soc. Chem. Ind., Basle*) produce shades similar to Turkey Red and very fast to washing and acid. They are dyed in a bath of sodium sulphate, sodium carbonate, and soap, and are diazotised, and then developed with  $\beta$ -naphthol. They are prepared by coupling diazo compounds with *m*-aminobenzoylaminonaphthol-sulphonic acids.

**Sulphone Azurine** is obtained from benzidinesulphonedisulphonic acid and 2 mol. of phenyl- $\beta$ -naphthylamine. The commercial product is a greyish blue powder which dissolves in water and alcohol with blue colours. The aqueous solution gives a blue precipitate with hydrochloric acid and also with sodium hydroxide. Concentrated sulphuric acid dissolves the dye, forming a violet solution from which blackish violet flocks separate on dilution with water.

It is better suited for the dyeing of wool (with sodium sulphate and sodium acetate) than of cotton. Closely related to it are Brilliant Sulphone Azurine, Sulphone Brown, and probably also the following dye.

**Sulphone Acid Blue B** (*Bayer*)<sup>1</sup> is a blue powder which dissolves in water with a violet-blue colour, and in alcohol with a blue colour. The colour of the aqueous solution is changed to greenish blue by hydrochloric acid, and to red by sodium hydroxide. Concentrated sulphuric acid produces a blue solution which becomes greenish blue on dilution.

Wool is dyed in a bath containing sodium sulphate and acetic acid.

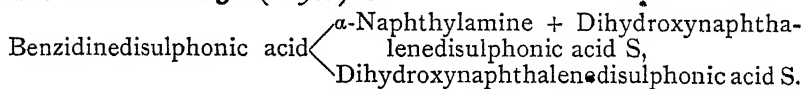
### 8. Polyazo Dyes.

**Benzo Black Blue G** (*Bayer*) is prepared from 1 mol. of benzidine-disulphonic acid, 1 mol. of  $\alpha$ -naphtholsulphonic acid NW, and 1 mol. of  $\alpha$ -naphthylamine; the resulting intermediate product is again diazotised and coupled with another molecule of  $\alpha$ -naphtholsulphonic acid NW. The commercial product is a black powder which is insoluble in alcohol but dissolves in water with a bluish black colour. The aqueous solution gives a blackish blue precipitate with hydrochloric acid and is coloured blue by sodium hydroxide. Concentrated sulphuric acid produces a blackish green solution, from which a precipitate is obtained on dilution.

Cotton is dyed blackish blue.

**Benzo Black Blue R** is derived from tolidine, and is similar to the preceding dye.

**Benzo Black Blue 5G** (*Bayer*) is



<sup>1</sup> *Rev. Gen. Mat. Col.*, 1898, 2, 26.

**Direct Black V** (*Sandoz*) is

Benzidine  $\left\{ \begin{array}{l} \text{Aminonaphtholsulphonic acid G,} \\ \text{2-Amino-8-naphthol-3 : 6-disulphonic acid} + \alpha\text{-Naphthylamine.} \end{array} \right.$

The commercial product is a greyish black powder which dissolves in water with a violet-black colour. The solution gives a bluish black precipitate with hydrochloric acid and is coloured reddish violet by sodium hydroxide. Concentrated sulphuric acid produces a blue solution from which a bluish black precipitate is obtained on dilution.

Unmordanted cotton is dyed in mauve-green to blackish violet shades in a neutral or faintly alkaline boiling bath containing 15 per cent. sodium chloride or anhydrous sodium sulphate. Also by diazotisation on the fibre and coupling with  $\beta$ -naphthol a dark navy blue is produced, or a bluish black by coupling with a diamine.

**Chloramine Black N** (*Sandoz*) is a dark powder with a bronze lustre. The deep bluish green aqueous solution gives a blue precipitate with hydrochloric acid, and a bluish green precipitate with sodium hydroxide. Concentrated sulphuric acid produces a blue solution from which a blue precipitate is obtained on dilution.

Unmordanted cotton and also half-wool and half-silk are dyed, in pale shades, grey, in 5 to 6 per cent., greenish black.

**Benzo Grey** (*Bayer*) is

Benzidine  $\left\{ \begin{array}{l} \text{Salicylic acid,} \\ \alpha\text{-Naphthylamine} + \alpha\text{-Naphtholsulphonic acid NW.} \end{array} \right.$

Cotton is dyed grey. The dye is a greenish black powder which dissolves in water with a reddish brown colour. The solution is not changed by sodium hydroxide; hydrochloric acid produces a black precipitate. Concentrated sulphuric acid produces a blue solution from which the dye is precipitated in black flocks on dilution with water.

**Benzo Indigo Blue** (*Bayer*) is

Tolidine  $\left\{ \begin{array}{l} \text{Dihydroxynaphthalenesulphonic acid S,} \\ \alpha\text{-Naphthylamine} + \text{Dihydroxynaphthalenesulphonic acid S.} \end{array} \right.$

It is a grey powder which dissolves easily in water with a violet colour. The aqueous solution is turned reddish violet by sodium hydroxide, and gives a bluish violet precipitate with hydrochloric acid. Concentrated sulphuric acid produces a greyish blue solution from which a violet-blue flocculent precipitate is obtained on dilution.

Cotton is dyed indigo blue.

To this class also belong Benzo Navy Blue, Benzocyanin, and Congo Fast Blue.

**Toledo Blue V** (*Leonhardt*)<sup>1</sup> also probably belongs to this group.

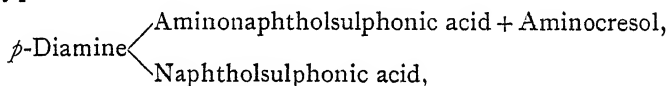
<sup>1</sup> *Rev. Gen. Mat. Col.*, 1898, 2, 419.

It is a greyish blue powder which easily dissolves in cold water with a blue colour. The aqueous solution is unchanged by sodium hydroxide, and gives a blue precipitate with hydrochloric acid. A greenish black solution is produced in concentrated sulphuric acid which on the addition of water assumes a violet-red and then a red colour, and finally deposits a dirty grey precipitate.

It dyes cotton directly when sodium sulphate and sodium carbonate or soap are added to the bath.

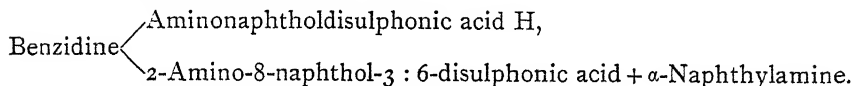
**Acetylene Blue 6B, 3B, BX, and 3R** (*Soc. Chem. Ind., Basle*)<sup>1</sup> dye cotton directly in a neutral bath in the presence of sodium sulphate. They dissolve in cold water with blue or violet colours. The aqueous solutions give blue or reddish blue (3R) precipitates with hydrochloric acid. Sodium hydroxide is without action on 6B, and colours a solution of 3B reddish, of BX reddish blue, and of 3R red. In concentrated sulphuric acid 6B produces greenish blue, 3B bluish green, BX and 3R blue, solutions.

**Indigen Blue BB, B, and R** (*Soc. Chem. Ind., Basle*)<sup>2</sup> are constituted on the type



and resemble the diaminogen dyes in their behaviour. They are employed in a boiling bath with sodium chloride or sodium sulphate and a little soap or sodium carbonate. The direct colours are dull and of no value. Greenish blue to reddish blue shades are produced, however, by diazotising and coupling with  $\beta$ -naphthol.

**Direct Indone Blue R** (*Sandoz*) is



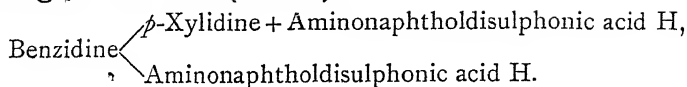
It is a bluish black powder which gives a bluish black solution in water. Hydrochloric acid produces a dark blue precipitate. Sodium hydroxide produces a violet solution. The blue solution in concentrated sulphuric acid yields a dark blue precipitate on dilution.

In a boiling bath containing 2 per cent. sodium carbonate, and 15 per cent. sodium sulphate or sodium chloride, unmordanted cotton is dyed in greyish blue to indigo blue colours which are very fast to washing and to light; the colours are rather redder than those produced by diamine black BH, and, like the latter, can be diazotised on the fibre and combined with phenols and amines, whereby dark blues and blacks are produced which are very fast to light and quite fast to washing.

<sup>1</sup> *Rev. Gen. Mat. Col.*, 1899, 3, 249.

<sup>2</sup> *Ibid.*, 1899, 3, 249.

**Melogen Blue 3H** (*Sandoz*) is



It is a bluish black powder which dissolves in water with a bluish violet colour. Hydrochloric acid produces a violet precipitate in the solution. Sodium hydroxide changes the colour of the solution to violet.

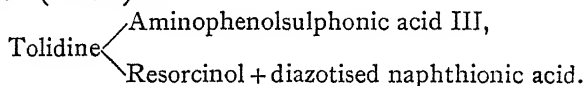
The blue solution in concentrated sulphuric acid gives a bluish violet precipitate on dilution.

In a neutral or faintly alkaline bath with the addition of 20 to 30 per cent. sodium chloride or sodium sulphate, melogen blue BH dyes unmordanted cotton an indigo-blue of a rather greener shade than that produced by diamine black BH. These direct colours can be diazotised and combined with  $\beta$ -naphthol, whereby a beautiful grey is produced with 1 to 2 per cent. of the dye, whilst with 6 per cent. a deep, moderately greenish black is produced which is quite fast to washing and very fast to light.

**Chloramine Blue 3G** and **HW** are dark powders with a bronze lustre which dissolve in water with a blue colour. The solutions give blue precipitates with hydrochloric acid or sodium hydroxide. Concentrated sulphuric acid produces a blue solution which yields a violet-blue precipitate on dilution.

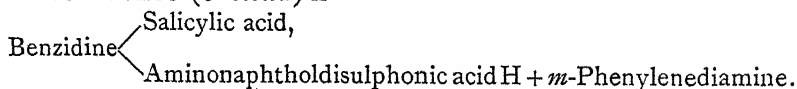
Brands 3G and HW are employed like chloramine green; on unmordanted cotton the former produces a greenish blue whilst mark HW gives a blackish blue. Both dyes are particularly suitable for dyeing mixed fabrics.

**Azo Corinth** (*Oehler*) is



The commercial product is a blackish brown powder which dissolves in water with a brownish red colour. The colour of the solution is changed to a more violet-red by sodium hydroxide. Hydrochloric acid produces a reddish brown precipitate. The violet-blue solution in concentrated sulphuric acid gives a brown precipitate on dilution. Unmordanted cotton is dyed brownish violet.

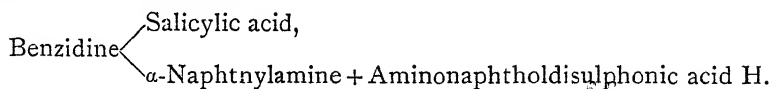
**Diamine Bronze** (*Cassella*) is



The commercial product is a black powder which dissolves in hot water with a brown colour. The colour of the solution becomes paler in the presence of sodium hydroxide; hydrochloric acid produces a

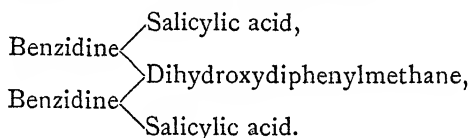
brown precipitate. The solution in concentrated sulphuric acid is brownish violet and yields a dark precipitate on dilution with water. Unmordanted cotton is dyed brown.

**Benzo Olive** (*Bayer*) is



It dyes unmordanted cotton in olive-green shades. The commercial product is a black powder which dissolves in water with a dark green colour. The solution is turned brown by sodium hydroxide, whilst hydrochloric acid precipitates the dye in blackish green flocks. The violet solution in concentrated sulphuric acid yields a greenish black precipitate on dilution.

**Mekong Yellow G** (*Durand, Huguenin, & Co.*) is



It dyes cotton greenish yellow in a soap bath. It is a brown powder which dissolves in water with a yellowish brown colour. The aqueous solution gives a brown precipitate with hydrochloric acid, and is reddened by sodium hydroxide. Concentrated sulphuric acid produces a violet solution which becomes turbid by the addition of water owing to the separation of brown flocks.

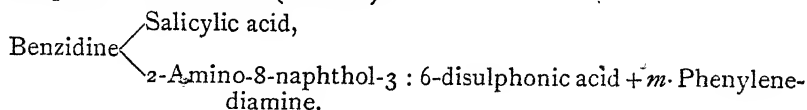
The dyes, Mekong Yellow R and Azo Orange R, manufactured by the same firm, are of a similar character.

**Benzo Chrome Brown 3R** (*Bayer*).<sup>1</sup>—The commercial product is a grey powder which is slightly soluble in alcohol and dissolves easily in water with an orange-brown colour. The aqueous solution gives a brown precipitate with hydrochloric acid and a reddish brown precipitate with sodium hydroxide. The blue solution in concentrated sulphuric acid gives a blue precipitate on dilution with water.

Stannous chloride and hydrochloric acid produce a brown precipitate which gradually becomes violet-black and dissolves in the acid.

It is suitable for dyeing unmordanted cotton. By subsequent treatment with potassium bichromate and copper sulphate very fast colours are obtained.

**Trisulphone Brown B** (*Sandoz*) is



<sup>1</sup> *Rev. Gen. Mat.*, 1893, 2, 421.



It is a greyish brown powder which dissolves in water with a coffee-brown colour. The solution yields a blackish brown precipitate with hydrochloric acid, and is turned reddish brown by sodium hydroxide. The bluish violet solution in concentrated sulphuric acid gives a dark brown precipitate on dilution.

In the presence of 2 per cent. sodium carbonate and 15 to 20 per cent. sodium chloride, trisulphone brown B dyes unmordanted cotton in beautiful, coffee-brown shades which are very fast to washing and light. The colour is materially improved by subsequent treatment in a boiling bath with 1 per cent. potassium bichromate and 2 per cent. copper sulphate.

In a neutral bath half-wool and also half-silk are dyed fairly uniformly; the animal fibres are dyed rather yellower.

**Trisulphone Brown G** and **GG** are dyes in the preparation of which tolidine and dianisidine respectively are used instead of benzidine. They give rather yellower shades than the preceding dye, but resemble it in their reactions and applications.

**Chlorazol Deep Brown B** (*Holliday*) is identical with trisulphone brown B except that the end component is *m*-tolylenediamine.

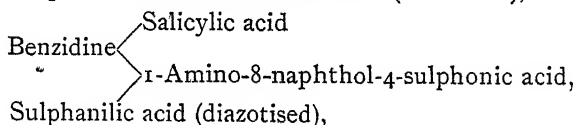
**Oxydiamine Orange G** and **R** (*Cassella*)<sup>1</sup> are brownish red powders which are sparingly soluble in cold water, but dissolve more readily in hot water with yellowish brown colours. The solutions give orange brown precipitates with hydrochloric acid and yellowish brown precipitates with sodium hydroxide. The solutions in concentrated sulphuric acid have an orange-brown colour, which becomes yellowish brown on dilution and give finally an orange-brown precipitate.

They are substantive cotton dyes but can also be employed on wool and silk.

**Diamine Green G** (*Cassella*), **Chlorazol Green G** (*Holliday*) are obtained by coupling diazotised *p*-nitroaniline and 1 mol. of aminonaphtholdisulphonic acid H, combining the product with 1 mol. of tetrazodiphenyl, and then adding 1 mol. of salicylic acid.

The commercial product is a black powder which dissolves in alcohol or water with a green colour. The solution becomes yellower in the presence of sodium hydroxide. Hydrochloric acid produces a dark precipitate. The violet solution in concentrated sulphuric acid gives a bluish black precipitate on dilution with water. Unmordanted cotton is dyed green.

A similar product is **Columbia Green** (*Akt. Ges.*), which is

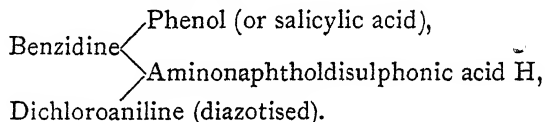


<sup>1</sup> *Rev. Gen. Mat. Col.*, 1899, 3, 249.

and probably also **Eboli Green** (*Leonhardt*) and **Benzo Dark Green B** (*Bayer*),<sup>1</sup> which is a greyish black powder soluble in cold water with a dark green colour; it gives a bluish green solution in alcohol. The colour of the solution becomes violet-black in the presence of sodium hydroxide; hydrochloric acid gives a blue, and in excess a black, precipitate. The blue solution in concentrated sulphuric acid gives a black precipitate on dilution. A mixture of stannous chloride and hydrochloric acid produces a blue precipitate which becomes black and slowly dissolves on warming, forming a colourless solution.

Cotton is dyed in dark green shades in a bath at the boiling point (one hour) containing 10 to 15 per cent. sodium sulphate. The colours can be destroyed by stannous chloride and zinc dust. The dye can also be used for dyeing half-wool in a neutral bath containing sodium sulphate. It can also be employed with silk and wool.

**Chloramine Green** (*Sandoz*) is



It is a dark powder with a pale bronze lustre and dissolves in water with a dark green colour. The aqueous solution gives a violet precipitate with hydrochloric acid, and becomes blackish green in the presence of sodium hydroxide. The violet solution in concentrated sulphuric acid gives a violet precipitate on dilution.

In a neutral or faintly alkaline bath chloramine green B dyes unmordanted cotton in bluish green shades, which are considerably brighter than those produced by diamine green B; it is also faster to alkali than the latter.

In a neutral bath it produces fine uniform colours on half-silk and half-wool; if the dyeing is too rapid, the animal fibres acquire a rather darker colour.

The following dyes probably also belong to the same class.

**Polyphenyl Black** (*Geigy*).

**Direct Deep Black G**<sup>2</sup> is a greyish black powder which dissolves in cold water with a brownish black colour. The aqueous solution gives a violet-black precipitate with hydrochloric acid, and a dirty violet-black precipitate with sodium hydroxide. The blue solution in concentrated sulphuric acid gives a precipitate of violet-black flocks on dilution with water.

It is a substantive dye and is suitable for dyeing cotton, half-wool, and jute. Cotton is dyed for one hour in a boiling bath containing 10

<sup>1</sup> *Rep. Gen. Mat. Col.*, 1899, 3, 56.

<sup>2</sup> *Ibid.*, 1899, 3, 124.

per cent. sodium chloride; for half-wool 15 to 20 per cent. sodium chloride or 20 to 25 per cent. sodium sulphate is added to the bath, and the dyeing is allowed to proceed for one and a half to two hours at the boiling point. The dye can also be diazotised on the fibre.

**Direct Deep Black RW** (*Bayer*)<sup>1</sup> is a grey powder which easily dissolves even in cold water with a violet-black colour. The solution gives a violet-black precipitate with hydrochloric acid, and a reddish blue precipitate with sodium hydroxide. The blue solution in concentrated sulphuric acid gives a reddish brown precipitate on dilution with water.

Cotton is dyed violet-black in a boiling bath with the addition of 5 to 15 per cent. of sodium chloride. The dye is also recommended for dyeing linen and especially jute. The colour can be discharged by stannous chloride and zinc dust. It forms a suitable base for aniline black.

**Direct Deep Black E** (*Bayer*)<sup>2</sup> is a blackish brown powder, which is sparingly soluble in cold water and dissolves easily in hot water with a brownish black colour. The aqueous solution gives a violet-black precipitate with hydrochloric acid, and is changed to bluish black by sodium hydroxide. Concentrated sulphuric acid produces a blue solution from which the dye is precipitated on dilution with water.

Cotton is dyed with the addition of sodium chloride to the bath.

**Direct Blue Black 2B** (*Bayer*)<sup>3</sup> is a brownish black powder, which is sparingly soluble in cold water but dissolves easily in hot with a bluish black colour. Blue precipitates are produced in the aqueous solution by hydrochloric acid or sodium hydroxide. The blue solution in concentrated sulphuric acid becomes turbid on the addition of water.

In the presence of sodium sulphate and some sodium carbonate, unmordanted cotton is dyed in very bright, blackish blue shades.

**Carbide Black BO** (*Soc. Chem. Ind., Basle*)<sup>4</sup> is a grey powder which is insoluble in alcohol, but dissolves in cold water and easily in hot water with a violet-black colour. Hydrochloric acid produces a violet-black precipitate, and sodium hydroxide a bluish red solution. The blue solution in concentrated sulphuric acid yields a bluish black precipitate on dilution. Stannous chloride and hydrochloric acid produce a bluish black precipitate which gradually dissolves to a colourless solution.

Cotton is dyed bluish black in the presence of sodium chloride. The colour is not very fast.

**Carbide Black RI** appears to have more satisfactory properties.

**Ebony Black** (*Soc. Chem. Ind., Basle*)<sup>5</sup> consists of a blackish brown

<sup>1</sup> *Rev. Gen. Mat. Col.*, 1899, 3, 125.

<sup>2</sup> *Ibid.*, 1898, 2, 418.

<sup>3</sup> *Ibid.*, 1899, 3, 248.

<sup>4</sup> *Ibid.*, 1899, 3, 57.

<sup>5</sup> *Ibid.*, 1899, 3, 56.

dye mixed with a small quantity of a blue dye. It is insoluble in alcohol but dissolves in cold water with a blackish blue colour. Hydrochloric acid produces a blue, sodium hydroxide a blackish blue, precipitate. The blue solution in concentrated sulphuric acid yields the dye in blue flocks on dilution with water. A mixture of stannous chloride and hydrochloric acid produces at first a blue precipitate, which quickly dissolves, forming a colourless solution.

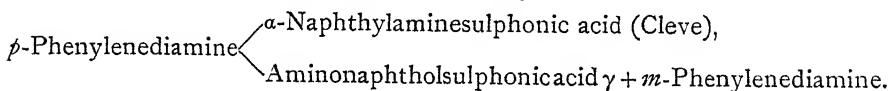
It can be used for dyeing cotton and half-wool; the former is dyed in greenish black shades in a bath of sodium carbonate and sodium sulphate. The dye can be diazotised on the fibre.

**Dark Blue 3B** (*Bayer*)<sup>1</sup> is a greyish black powder which dissolves in cold water with a violet-black colour. The aqueous solution gives a bluish black precipitate with hydrochloric acid, and a violet-black precipitate with sodium hydroxide. Concentrated sulphuric acid produces a blue solution which gives a blue precipitate on dilution with water.

Cotton is dyed directly in a bath containing 10 per cent. sodium sulphate and 1 per cent. sodium carbonate; on diazotisation on the fibre and development with  $\beta$ -naphthol, etc., the dyeings are fast to washing.

**Diazo Blue 3R** (*Bayer*)<sup>2</sup> is a substantive cotton dye, the direct dyeings of which, however, are valueless. By diazotising on the fibre and developing with  $\beta$ -naphthol a very pure blue with a reddish tinge is produced, which, especially in conjunction with Diazo Indigo Blue B, is suitable for the production of indigo shades. The dye is used in the presence of sodium chloride. The commercial product is a dark brown powder which dissolves in water with a reddish blue colour. The aqueous solution gives a blue precipitate with hydrochloric acid, and acquires a yellowish red colour in the presence of sodium hydroxide. Concentrated sulphuric acid produces a blue solution which gives a blue precipitate on dilution with water.

**Columbia Black FF extra** (*Akt.-Ges.*)<sup>3</sup> is



It is a brownish black powder which dissolves in water with a violet-black colour, and is insoluble in alcohol. Sodium hydroxide and hydrochloric acid produce violet precipitates in the aqueous solution. The blue solution in concentrated sulphuric acid becomes turbid on dilution with water owing to the separation of a violet precipitate. Stannous chloride and hydrochloric acid produce a violet precipitate, which dissolves slowly in the cold, forming a colourless solution.

<sup>1</sup> *Rev. Gen. Mat. Col.*, 1899, 3, 124.

<sup>2</sup> *Ibid.*, 1899, 3, 419.

<sup>3</sup> *Ibid.*, 1899, 3, 284.

Cotton is dyed bluish black from a boiling bath containing sodium sulphate and sodium carbonate.

This class also includes the following few dyes, which are obtained by the action of diazo- and tetrazo-compounds on phenylene- or tolylenediamines and their sulphonic acids, and dye unmordanted cotton brown:—

**Tolylene Brown, Benzo Brown G, Cutch Brown, Benzo Dark Brown, Benzo Black Brown, Direct Brown T, Diamine Catechin, Pegu Brown, Leather Brown, etc.**

**Azo Dyes applicable for the so-called "Two-bath Process."**—In this process the dyes are fixed on the fibre and coupled with a diazo-compound. The first dyeing is effected, as usual, in the presence of sodium sulphate, sodium carbonate, etc. The fabric is then passed for about thirty minutes through a solution of a diazo-compound (generally *p*-nitrodiazobenzene chloride) at the ordinary temperature. The colours produced in this way are usually darker, and are particularly fast to light and to washing.

Of dyes, suitable for this purpose, mention may be made of Chloramine Orange, Benzo Brown, Tolylene Orange, Direct Black, Pluto Black, Chicago Blue, Chrysamin, Congo Brown, Columbia Brown, Chromanil Brown R2G, Zambesi Black DR, O, Columbia Black, etc.

Special brands are brought on the market by many firms; for example:—

**Diamine Nitrazol Browns G, B, RD, BD (Cassella).**—Brands RD and BD can also be employed without subsequent coupling.

**Benzo Nitrol Brown G (Bayer).**<sup>1</sup>—The commercial product is a brown powder which is slightly soluble in alcohol, but dissolves in hot water with an orange-brown colour. The aqueous solution gives a bluish red precipitate with hydrochloric acid, and an orange-red precipitate with sodium hydroxide. The dye dissolves in concentrated sulphuric acid with a blue colour; on diluting the solution with water, a bluish black precipitate is obtained.

Although unmordanted cotton can be dyed directly, the dyeings have no practical value. By treating them, however, in a bath of *p*-nitrodiazobenzene, their fastness is materially increased.

**Benzo Nitrol Brown 2R (Bayer)**<sup>2</sup> is an analogous dye, which is likewise fixed on the fabric and coupled with *p*-nitrodiazobenzene.

It is brought on the market in the form of a brown powder with a bronze lustre, which is slightly soluble in cold water, but dissolves more easily in hot water with an orange-brown colour. The aqueous solution gives a brown precipitate with hydrochloric acid and an orange-brown precipitate with sodium hydroxide. Concentrated sulphuric acid produces a bluish red solution which, on dilution with water, gives a

<sup>1</sup> *Rev. Gen. Mat. Col.*, 1898, 2, 460.

<sup>2</sup> *Ibid.*, 1898, 2, 460.

blue precipitate, finally acquiring a reddish brown colour in the presence of an excess of water.

**Benzo Nitrol Dark Brown N** (*Bayer*).

**Benzo Nitrol Brown 5B** (*Bayer*).<sup>1</sup>—The commercial product is a brown powder which easily dissolves in warm water with a yellowish brown colour. The aqueous solution gives a yellowish brown precipitate with hydrochloric acid, and becomes more orange-yellow in the presence of sodium hydroxide. Concentrated sulphuric acid produces a blue solution from which water precipitates a brownish black substance. Stannous chloride and hydrochloric acid produce at first a yellowish brown precipitate which gradually dissolves; the solution is decolorised by boiling. The dye dissolves slightly in alcohol with a brownish yellow colour.

The dye is employed in the presence of sodium carbonate and sodium sulphate. The colour becomes materially faster by subsequent treatment with potassium bichromate and copper sulphate.

This class includes also Dianil Black (*M. L. Br.*), which is identical with Cuba Black R (*Petersen*), Naphthylamine Indigo RF, and Naphthylamine Dark Blue R (*Kalle*).

### 9. Azostilbene Dyes.

Azostilbenesulphonic acid and its derivatives may also be classified with the azo dyes. Until recently they were considered to be essentially azoxy-dyestuffs, but Green and his pupils<sup>2</sup> have shown that they are all azo-compounds.

**Sun Yellow, Afghan Yellow** (*Holliday*), **Curcumin S, Direct Yellow RT; Direct Yellow J** (*Poirrier*), **Azidine Fast Yellow G** (*Jäger*), **Naphthylamine Yellow, etc.**, are obtained by warming *p*-nitrotoluenesulphonic acid with sodium hydroxide. The commercial products are brown powders, which are insoluble in alcohol, but dissolve easily in water with a reddish yellow colour. Hydrochloric acid and sodium hydroxide produce brownish yellow precipitates in the aqueous solution. Concentrated sulphuric acid dissolves the dyes with reddish violet or red colours; the dye is precipitated on dilution. Golden-yellow shades are produced on unmordanted cotton in the presence of sodium chloride, and on silk and wool in an acid bath.

Similar dyestuffs are:—Chicago Orange G and KR (*Geigy*), Arnica Yellow (*Geigy*), the Mikado colours (*Leonhardt*) (Mikado Orange, Mikado Yellow, Mikado Brown), Renol Yellow R (*Ter Meer*), and Direct Yellow R (*Bayer*).<sup>3</sup>

**Diphenyl Yellow** (*Geigy*)<sup>4</sup> is a pale reddish brown powder which gives a turbid, brownish yellow solution in water. A darker solution

<sup>1</sup> *Rev. Gen. Mat. Col.*, 1898, 2, 421.

<sup>3</sup> *Rev. Gen. Mat. Col.*, 1898, 2, 458.

<sup>2</sup> *J. Soc. Dyers and Col.*, 1907, 23, 162.

<sup>4</sup> *Ibid.*, 1898, 2, 68.

is produced in hydrochloric acid or sodium hydroxide. Concentrated sulphuric acid produces a reddish brown solution. Cotton is directly dyed pale yellow in a boiling bath with the addition of sodium sulphate. The colour is rendered fast to alkali by subsequent treatment with potassium bichromate.

**Diphenylcitronin G** (*Geigy*)<sup>1</sup> is a pale reddish brown powder which dissolves in water with a pale yellow colour. The solution is unchanged by sodium hydroxide, and becomes rather lighter in colour in the presence of hydrochloric acid. Concentrated sulphuric acid dissolves the dye with a reddish brown colour.

### III. THIAZOLE DYES.

By heating *p*-toluidine and its homologues, for example *as-m*-xylidine, with sulphur, thiazole derivatives (dehydrothio-*p*-toluidine, dehydrothio-*m*-xylidine, primuline, and homologues) are obtained, which are either used directly as dyes in the form of sulphonic acids or serve as the materials from which very valuable dyes are produced.

**Primuline** (Thiochromogen, Polychromine, Aureoline, Sulphine, etc.) is prepared by heating *p*-toluidine and an excess of sulphur at a high temperature and subsequently sulphonating the resulting primuline base. The commercial product is the sodium salt, and is a yellow powder which dissolves in water with a pale yellow colour. The aqueous solution is unchanged by sodium hydroxide, and gives a yellow precipitate with hydrochloric acid. Concentrated sulphuric acid produces a yellow, fluorescent solution, from which a green precipitate is obtained on dilution with water.

Unmordanted cotton is dyed yellow.

Primuline is not very largely employed as a yellow dye, but its properties are utilised in another direction. The dye on the cotton can be converted by treatment with nitrous acid into a diazo compound, from which very diverse shades of colour can be produced directly on the fabric by the action of phenols or amines.

Primuline Red is produced by the action of  $\beta$ -naphthol.

**Chromine G** (*Kalle*) is obtained by heating dehydrothiotoluidine and sulphur, and subsequently methylating and sulphonating the product; it cannot be diazotised. It is a brown powder which dissolves in hot water with a brownish yellow colour. Hydrochloric acid and sodium hydroxide precipitate the dye in brownish yellow or greenish yellow flocks. Concentrated sulphuric acid produces a yellow, fluorescent solution from which a flocculent, brown precipitate is obtained on dilution with water.

It dyes cotton and half-silk in an alkaline bath.

**Thioflavine T** (*Cassella*).—When dehydrothiotoluidine is treated

<sup>1</sup> *Rev. Gen. Mat. Col.*, 1898, 2, 68.

with methyl chloride or with methyl alcohol and hydrochloric acid, the first action results in the replacement of the aminic hydrogen atoms by methyl groups; finally, however, a quaternary ammonium compound is formed. The chloride of this is a fine yellow dye, which is soluble in water; it is brought on the market under the name "Thioflavine." Thioflavine is fixed after the manner of basic dyes on tannin-mordanted cotton, and produces a greenish yellow similar to that of auramine.

Silk is dyed greenish yellow from an acid, boiled-off liquor bath.

The commercial product is a yellow, crystalline powder, which dissolves in water and in alcohol with a yellow colour. The alcoholic solution shows a green fluorescence. The solution is not affected by hydrochloric acid or sodium hydroxide. Concentrated sulphuric acid produces a colourless solution which becomes yellow on dilution.

**Thioflavine S** is the sodium salt of a sulphonic acid of methylated primuline; it is a yellow powder which is easily soluble in water. The alcoholic solution shows a green fluorescence. The yellow, aqueous solution gives an orange-yellow precipitate with hydrochloric acid and is unchanged by sodium hydroxide. The brown solution in concentrated sulphuric acid yields an orange-yellow precipitate on dilution with water.

It dyes unmordanted cotton greenish yellow.

**Chloramine Yellow M** (*Bayer*), **Chlorophenine**, or **Oxyphenine** (*Clayton*), is obtained by oxidising an alkaline solution of dehydrothiolumidinesulphonic acid with bleaching powder, lead peroxide, etc. It dyes wool and unmordanted cotton in very fast, yellow shades. The commercial product is a yellowish brown powder which dissolves in water with a yellow colour. Hydrochloric acid and sodium hydroxide produce orange-yellow precipitates. The red solution in concentrated sulphuric acid gives a brown precipitate on dilution with water.

Chloramine Orange (*Bayer*) and Chloramine Brown are similar dyestuffs.

**Chloramine Yellow GG** (*Bayer*)<sup>1</sup> is an orange-brown powder which dissolves in water with a yellow colour. Hydrochloric acid and sodium hydroxide produce brownish yellow precipitates in the aqueous solution. The dye dissolves in concentrated sulphuric acid with a brownish yellow colour, and is recovered on dilution as a reddish yellow precipitate.

It dyes cotton in greenish yellow shades in a boiling bath containing sodium chloride.

**Thiazole Yellow** (*Bayer*), **Clayton Yellow** (*Clayton*), or **Mimosa** (*Geigy*), is obtained by the action of ammonium hydroxide on diazotised primuline and also by the action of dehydrothiolumidinesulphonic acid on the diazo compound of the same acid. It is a yellow

<sup>1</sup> *Rev. Gen. Mat. Col.*, 1900, 4, 8.



powder which dissolves in water and in alcohol with a yellow colour. The aqueous solution gives reddish yellow precipitates with hydrochloric acid and sodium hydroxide. Concentrated sulphuric acid produces a brownish yellow solution.

It dyes unmordanted cotton yellow in a soap bath.

**Oriol Yellow** (*Geigy*), **Cotton Yellow R** (*B.A.S.F.*), **Alkali Yellow** (*Dahl*), obtained from diazotised primuline and salicylic acid, is a red powder which dissolves in water with an orange-red colour. Hydrochloric acid and sodium hydroxide produce in the aqueous solution yellow or orange-yellow precipitates. The red solution in concentrated sulphuric acid becomes turbid on dilution with water owing to the separation of brownish yellow flocks.

**Yellow R** (*B.A.S.F.*) and **Alkali Yellow** (*Dahl*).—If the coupling is effected with *m*-phenylenediamine instead of salicylic acid, **Alkali Brown R** is obtained, which dyes unmordanted cotton brown and behaves like oriol yellow towards reagents. **Terracotta F** (*Geigy*), **Cotton Orange R** (*B.A.S.F.*), and **Diamine Fast Yellow A** (*Cassella*) are dyestuffs of a similar type.

**Nitrophenine** (*Clayton*) is obtained by coupling *p*-nitrodiazobenzene with dehydrothio-*p*-toluidinesulphonic acid, and dyes unmordanted cotton greenish yellow. The commercial product is a brown powder which dissolves in water with a reddish yellow colour. The solution gives a yellow precipitate with hydrochloric acid, and is turned violet by sodium hydroxide. Concentrated sulphuric acid produces a yellow solution which gives a yellow precipitate on dilution with water.

**Curcuphenine Yellow** (*Clayton*)<sup>1</sup> is a brownish red powder which dissolves in water with an orange-yellow colour and gives a violet solution in alcohol. The aqueous solution is turned brown by hydrochloric acid, and gives a flocculent precipitate with sodium hydroxide. Concentrated sulphuric acid produces a reddish brown solution.

Unmordanted cotton is dyed in a bath of sodium chloride. Chlorophenine Orange R and 2R<sup>2</sup> are similar dyestuffs.

**Dianil Yellow G**, **3G**, and **R** (*M. L. Br.*)<sup>3</sup> are substantive monoazo-dyes, which are prepared from primuline or dehydrothiotoluidine and a  $\beta$ -diketone (ethyl acetoacetate). The brand G gives a more greenish yellow than chrysophenin, whilst brand 3G gives a very greenish yellow. Cotton is dyed in the presence of sodium chloride or sodium sulphate. Brand G is a brown powder, which is slightly soluble in cold water but dissolves easily in hot water with a yellowish brown colour. The aqueous solution gives an orange precipitate with hydrochloric acid and a violet-red precipitate with sodium hydroxide. Stannous chloride

<sup>1</sup> *Rev. Gen. Mat. Col.*, 1897, 1, 81.

<sup>2</sup> *Ibid.*, 1897, 1, 81.

<sup>3</sup> *Ibid.*, 1899, 3, 197.

and hydrochloric acid produce an orange-yellow precipitate which dissolves by warming. The yellow solution in concentrated sulphuric acid yields a yellow precipitate on dilution with water. The dye dissolves slightly in alcohol with a yellow colour.

Brand 3G is a dirty yellow powder which dissolves in cold water. Hydrochloric acid produces an orange, and sodium hydroxide an orange-yellow, precipitate. The dye is insoluble in alcohol, and its behaviour with stannous chloride and hydrochloric acid and with concentrated sulphuric acid is the same as that of brand G.

Brand R is an orange-yellow powder which is easily soluble in water and shows reactions similar to those of the two preceding dyes.

**Erika B** (*Akt. Ges.*) is a reddish brown powder obtained from diazotised dehydrothio-*m*-xyldine and  $\alpha$ -naphthol-3:8-disulphonic acid; it dissolves in water and in alcohol with a red colour. The aqueous solution gives a red precipitate with hydrochloric acid, and a bluish red precipitate with sodium hydroxide. Concentrated sulphuric acid produces a red solution which yields a red precipitate by dilution.

Unmordanted cotton is dyed a very beautiful rose colour.

**Diazo Brilliant Scarlet** (*Bayer*) is prepared by condensing 2-amino-5-naphthol-7-sulphonic acid with *m*-nitrobenzaldehyde, heating the product with sulphur and sodium sulphide whereby the thiazole compound is formed, and then treating this with a diazo-compound.

The following dyes also belong to this class:—**Salmon Red**, **Emin Red**, **Erika 2GN**, **4GN**, of the same firm;<sup>1</sup> **Geranin BB** and **G**, **Brilliant Geranin B** and **3B** (*Bayer*); **Titan Rose** (*Read Holliday*); prepared from diazotised dehydrothiotoluidine and  $\beta$ -naphthol-6-sulphonic acid **S**); **Clayton Cloth Red** (from diazotised dehydrothio-*p*-toluidinesulphonic acid and  $\beta$ -naphthol); **Thiazin Red G** and **R**; **Thiazin Brown G** and **R** (*B.A.S.F.*).

#### IV. PYRAZOLONE DYES.

**Tartrazine** is the most important representative of this class. It is obtained by the action of 1 mol. of dihydroxytartaric acid on 2 mol. of *p*-phenylhydrazinesulphonic acid. It is an orange powder which dissolves easily in water with a golden-yellow colour. The colour of the solution is darkened by sodium hydroxide, but is not affected by hydrochloric acid. Concentrated sulphuric acid produces a yellow solution.

It dyes wool and silk yellow in an acid bath. The colours on wool are very fast.

A dyestuff, similar to tartrazine but of unknown composition, is brought on the market under the name **Flavazine S** (*M. L. Br.*);<sup>2</sup> like tartrazine, it is employed on wool in a bath containing sodium hydrogen

<sup>1</sup> *Z. anorg. Chem.*, 1896, 9, 679.

<sup>2</sup> *Rev. Gen. Mat. Col.*, 1900, 4, 93.

sulphate (tartar substitute), but equalises better. It is an orange-yellow powder which is soluble in water. The aqueous solution gives orange precipitates with hydrochloric acid and sodium hydroxide. Concentrated sulphuric acid produces a yellowish brown solution from which the dye is precipitated in yellow flocks on dilution.

Probably Oehler's **Hydrazine Yellow O**, which produces rather greener shades than tartrazine, and also **Light-fast Yellow 3G** (*Bayer*) belong to this class.

## V. DIPHENYL- AND TRIPHENYL-METHANE DYES.

### 1. Diphenylmethane Dyes.

**Auramine** is a yellow basic dye which produces pure yellow shades on tannin-mordanted cotton; it can also be used for dyeing leather and paper. The commercial product, the hydrochloride of a colourless base, is a yellow powder which dissolves in warm water with a pale yellow colour. The solutions become dark yellow in the presence of hydrochloric acid. The dye is decomposed by boiling acids into ammonia and tetramethyldiaminobenzophenone. The aqueous solution gives with sodium hydroxide a white precipitate which is soluble in ether. The solution in concentrated sulphuric acid is colourless but becomes yellow on dilution.

The dye is prepared by heating tetramethyldiaminodiphenylmethane, sulphur, sodium chloride, and ammonium chloride in a current of ammonia under slightly increased pressure.

**Auramine G** dyes tannin-mordanted cotton in greener shades than does ordinary auramine, but in other respects resembles it in its behaviour with reagents. It is obtained by heating a mixture of dimethyldiaminodi-*o*-tolylmethane, sulphur, sodium chloride, and ammonium chloride in a current of ammonia.

(For its volumetric analysis by means of acid dyestuffs, see Pelet and Garuti.<sup>1</sup>)

The dye is decomposed into ammonia and dimethyldiaminodi-*o*-tolyl ketone by heating with acids.

Phenylauramine is put on the market under the name **Arnicanine**, but is very seldom used on account of its slight solubility in water. It dyes tannin-mordanted cotton in brown shades.

**Pyronine G** is produced by the oxidation of tetramethyldiaminodiphenylmethane oxide. The commercial product dissolves in water and in alcohol with a red colour. The strongly fluorescent aqueous solution becomes paler in the presence of hydrochloric acid. Sodium hydroxide produces a red precipitate. The yellowish red solution in concentrated sulphuric acid becomes redder on dilution.

<sup>1</sup> *Z. Farb. Ind.*, 1908, 7, 44.

The dye is employed on cotton, wool, and silk.

**Pyronine B** is the corresponding ethyl derivative; it resembles brand G but produces more bluish colours.

**Acridine Red** is produced by the careful oxidation of pyronine B.

## 2. Triphenylmethane Dyes.

**Malachite Green** (Bitter Almond Oil Green, New Victoria Green, Fast Green, Diamond Green<sup>2</sup>B, etc.).

*Preparation.*—By heating benzaldehyde and dimethylaniline with a condensing agent tetramethyldiaminotriphenylmethane, the leuco base corresponding with malachite green, is obtained, and is transformed into the dyestuff by oxidation with lead peroxide.

Like rosaniline, the colourless base forms coloured salts with acids, water being eliminated.

The oxalate and the zinc chloride double salt crystalline well. The commercial article usually consists of large, greenish, metallic-looking leaflets (oxalate) or yellow, prismatic crystals (zinc chloride double salt). The salts dissolve easily in water and in alcohol with magnificent green colours. From the solution the colourless base is precipitated, immediately by alkali hydroxides, slowly by sodium carbonate and ammonium hydroxide. The colour is changed by strong mineral acids through yellowish green to a dirty yellowish brown. The base, liberated from its salts, gives at first a fairly colourless solution in dilute acids, but on warming the formation of the dyestuff commences.

The dye is converted into the corresponding leuco base by reduction. Malachite green differs from the otherwise very similar methyl green in that its colour does not change to violet on heating, as does that of the latter. The two substances on dyed fabrics can be distinguished from one another by means of this property.

Malachite green is a very powerful, beautiful dye. Wool is dyed directly, cotton after being mordanted with tannin.

The analysis can also be carried out by titration with titanous chloride.<sup>1</sup>

**Brilliant Green** (Malachite Green G, Diamond Green G, Ethyl Green).

From the chemical point of view this dye differs from the preceding in that it contains ethyl groups instead of methyl groups. It is obtained by the action of diethylaniline on benzaldehyde and oxidation of the resulting leuco base.

Brilliant green is usually brought on the market in the form of its crystalline sulphate; it dyes a yellower shade than malachite green.

**New Fast Greens 2B and 3B** are prepared from dichlorobenzalde-

<sup>1</sup> Cf. Knecht, *J. Soc. Dyers and Col.*, 1905, 21, 293.

hyde or a mixture of chloro- and dichloro-benzaldehyde and dimethylaniline. They dissolve in hot water with greenish blue colours and the solutions gelatinise on cooling. They produce bluer shades than malachite green.

**Glacier Blue**, obtained from dichlorobenzaldehyde and methyl-*o*-toluidine, gives very pure shades on silk.

**Setocyanine**, (*Geigy*),<sup>1</sup> prepared from *o*-chlorobenzaldehyde and monoethyl-*o*-toluidine, is a blue-grey powder which dissolves in water with a greenish blue colour. The solution gelatinises on cooling. Hydrochloric acid changes the colour of the solution to yellowish green, and in excess to brownish yellow. Sodium hydroxide produces a brownish yellow precipitate which dissolves in ether with a yellow colour. Concentrated sulphuric acid produces a brownish yellow solution which becomes yellowish green by dilution with water.

In an acid bath it dyes silk in rather less greenish shades than glacier blue.

**Setoglaucine** (*Geigy*),<sup>2</sup> prepared from *o*-chlorobenzaldehyde and dimethylaniline, is a blue-grey powder which dissolves in water with a greenish blue colour, and dyes silk a very pure blue-green in an acid-bath. The aqueous solution becomes yellowish green by the addition of hydrochloric acid, and brownish yellow in the presence of an excess of the acid. Sodium hydroxide produces a blue precipitate in the cold. The brownish yellow solution in concentrated sulphuric acid becomes yellowish green by dilution with water.

**Light Green SF Yellowish** differs essentially from the preceding, in that it is the salt of a sulphonic acid and is employed in an acid bath after the manner of acid dyes.

For its preparation dibenzyl-diethyldiaminotriphenylmethane, obtained from benzylolethylaniline and benzaldehyde, is converted by treatment with sulphuric acid into a sulphonic acid which is then oxidised to the dyestuff.

It produces a yellowish green shade.

The commercial product is a pale green powder which dissolves in water and in alcohol with a green colour. The aqueous solution becomes yellowish brown in the presence of hydrochloric acid, and is decolorised and rendered turbid by sodium hydroxide. Concentrated sulphuric acid produces a yellow solution which becomes green on dilution. A similar dye is **Light Green SF Bluish**, which is produced from benzylmethylaniline and yields rather bluer shades.

**Guinea Green B** is obtained by condensing benzaldehyde and benzylolethylanilinesulphonic acid and oxidising the resulting leuco compound.

**Guinea Green BV** is a derivative of *m*-nitrobenzaldehyde.

<sup>1</sup> *Rev. Gén. Mat. Col.*, 1899, 3, 173.

<sup>2</sup> *Ibid.*, 1899, 3, 173.

**Patent Blue V** (*M. L. Br.*),<sup>1</sup> like all brands of Patent Blue, is a derivative of *m*-hydroxybenzaldehyde. The commercial product is the magnesium or sodium salt of *m*-hydroxytetraethyldiaminotriphenylcarbinoldisulphonic acid (or of the sultonesulphonic acid); it is a brownish red powder which dissolves in water with a blue colour. Hydrochloric acid produces initially a green, and then a yellow, coloration. The solution is unchanged by sodium hydroxide. Concentrated sulphuric acid produces a yellowish solution which becomes yellow and then green on dilution.

Wool is dyed greenish blue from an acid bath. The colours are characterised by their fastness to alkali.

**New Patent Blue B** (*Bayer*)<sup>2</sup> is a blue-grey powder which dissolves in cold water with a greenish blue colour. The dye is only sparingly soluble in alcohol. The aqueous solution is turned greenish yellow by hydrochloric acid, whilst sodium hydroxide produces a blue precipitate. The yellow solution in concentrated sulphuric acid becomes orange-yellow and then greenish yellow on dilution.

The dye equalises well.

**New Patent Blue 4B** (*Bayer*)<sup>3</sup> is a reddish blue powder which dissolves in water with a blue colour. The aqueous solution becomes yellow on the addition of hydrochloric acid, and gives a brown precipitate with sodium hydroxide. Concentrated sulphuric acid produces a yellow solution which becomes greenish yellow on dilution. The dye is slightly soluble in alcohol.

**Patent Blue A**, the calcium salt of *m*-hydroxydibenzyl-diethyldiaminotriphenylcarbinoldisulphonic acid, is a similar dye.

**Cyanine B**, obtained by the action of suitable oxidising agents on patent blue V, is faster to light and to alkali than this, and dyes wool in indigo-blue shades.

**Cyanol** (*Cassella*) is produced by the condensation of *m*-hydroxybenzaldehyde and 2 mol. of monoethyl-*o*-toluidine, sulphonation of the leuco base, and oxidation of the resulting disulphonic acid. It dyes wool blue from an acid bath. The commercial product is a dark blue powder which dissolves in water with a blue colour. The solution becomes green and then yellow by the addition of hydrochloric acid. Sodium hydroxide produces a red solution on warming. The yellow solution in concentrated sulphuric acid becomes green and then blue on dilution.

**Cyanol FF** is also a dyestuff of this type, which produces purer shades on wool and silk from an acid bath than the preceding brands.<sup>4</sup>

**Cyanol Green B** (*Cassella*)<sup>5</sup> is a bluish green powder which dissolves

<sup>1</sup> Cf. also *Annalen*, 1897, 294, 377.

<sup>3</sup> *Ibid.*, 1898, 2, 421.

<sup>2</sup> *Rev. Gen. Mat. Col.*, 1898, 2, 421.

<sup>4</sup> *J. Soc. Dyers and Col.*, 1899 15, June.

<sup>5</sup> *Rev. Gen. Mat. Col.*, 1900, 4, 463.

in water with a bluish green colour. The colour of the aqueous solution is not changed by sodium hydroxide, but becomes brownish yellow in the presence of hydrochloric acid. Concentrated sulphuric acid produces a brownish yellow solution, which becomes at first reddish brown and then brownish yellow on dilution.

It dyes wool in bluish green shades in a bath containing sulphuric acid and sodium sulphate.

**Erioglaucine** (*Geigy*) is prepared from benzaldehyde-*o*-sulphonic acid and 2 mol. of benzyloethylanilinesulphonic acid; it is the ammonium salt of the anhydride of dibenzyl-diethyl-diamino-triphenylcarbinol-*o*:*p'*:*p''*-trisulphonic acid.

It dyes silk and wool from an acid bath in bluish green shades which are fast to alkali, and it exhausts well from the bath.

**Setopaline** is a closely related dye.

**Fast Green extra Bluish** (*Bayer*) is a blue-green, crystalline powder which dissolves in water and in alcohol with a greenish blue colour. The solution is turned yellow by hydrochloric acid and is decolorised by sodium hydroxide on warming. Concentrated sulphuric acid produces a yellowish red solution which becomes greenish blue on dilution.

**Chrome Green** (*Bayer*) is obtained by oxidising the condensation product of tetramethyldiaminobenzhydrol and benzoic acid. The commercial product is a brown powder which dissolves in water and in alcohol with a greenish blue colour. The solution becomes yellow in the presence of hydrochloric acid, and is decolorised by sodium hydroxide. Concentrated sulphuric acid produces an orange-yellow solution. Chromed wool is dyed green.

**Chrome Violet** (*Bayer*) is prepared like chrome green, using salicylic acid instead of benzoic acid. The commercial product is a black paste which is insoluble in water. Hydrochloric acid produces a reddish brown solution; sodium hydroxide forms a violet-red solution together with a dark precipitate. Concentrated sulphuric acid produces a yellowish brown solution which becomes reddish brown on dilution. Chromed wool is dyed violet.

**Ketone Blues G, R, and 4BN** (*M. L. Br.*) are obtained by condensing *m*-methoxybenzoic acid and tertiary amines in the presence of phosphoryl chloride.

**Azo Green** is an azo dye which dyes chromed wool green. It is prepared by oxidising the product obtained by coupling salicylic acid with diazotised *m*-aminotetramethyl-*p*-diaminotriphenylmethane. The commercial product is a green paste which is sparingly soluble in water and in alcohol. It dissolves in sodium hydroxide on warming; hydrochloric acid produces a brownish red colour. Concentrated sulphuric acid produces a brownish red solution which gives a brown precipitate on dilution.

**Rosaniline** (Triaminotolyldiphenylcarbinol) in the pure state forms colourless leaflets which become red in the air. Towards acids it behaves like a moderately strong base and forms salts with the elimination of water.

The base is reprecipitated from the solutions of its salts by the addition of alkalis. The precipitation is effected more slowly by ammonium hydroxide than by sodium hydroxide or potassium hydroxide. On the other hand, rosaniline expels ammonia from a boiling solution of ammonium chloride and is slowly converted into the chloride.

The monoacidic salts of rosaniline are mostly rather sparingly soluble in water. These solutions, however, exhibit a deep red colour in consequence of the extremely intense colouring power of the salts. The base itself is almost insoluble in cold water but dissolves appreciably in hot water; it separates again almost completely on cooling in the form of fragile colourless leaflets.

The **Hydrochloride**, **Acetate**, and the free **Base** are brought on the market. The first, under the name magenta, is directly employed as a dyestuff, and more rarely the second, whilst the last is used only in the production of aniline blue.

The commercial product (usually a mixture of homologues), which is exclusively employed in the manufacture of aniline blue, consists of usually more or less reddish brown crystalline leaflets. Its examination involves a dye trial and an estimation of the water at 100°. Since many kinds of rosaniline, however, are unsuitable for the production of blue even though they survive these tests, it is also necessary to ascertain their applicability in this direction.

Concentrated acids—for example, hydrochloric acid—colour rosaniline yellow; the red colour is reproduced by water. Aqueous solutions of rosaniline salts give a brownish red precipitate with alkalis and a splendid red precipitate with tannin.

When the solution after treatment with an alkali is shaken with ether, the latter acquires a yellowish brown fluorescence; the magenta-red colour is restored by shaking the ethereal solution with dilute acetic acid. Sulphurous acid decolorises rosaniline; the colour is regenerated, however, by exposing the solution to the air for a long time.

Rosaniline is prepared by oxidising a mixture of aniline and toluidine with arsenic acid or, more generally, nitrobenzene. By this means a mixture of aniline and *p*-toluidine yields pararosaniline, whilst ordinary rosaniline is produced if *o*-toluidine is simultaneously present.

Pararosaniline, together with its higher homologues, is employed in the manufacture of aniline blue, and is a commercial article. The recognised method of examination is a trial fusion for blue. Aniline blue, produced from pararosaniline, is characterised by a much purer



and greener shade than diphenylrosaniline, and has almost entirely displaced diphenylamine blue. It can be analysed by titration with titanous chloride.<sup>1</sup>

With regard to the examination of rosaniline and pararosaniline, Lambrecht and Weil<sup>2</sup> make the following statement:—

Commercial rosaniline is soluble in 20 volumes of approximately 30 per cent. hydrochloric acid on warming. The solution does not yield a deposit by cooling even after being kept for a day, whilst pararosaniline by the same treatment forms the sparingly soluble hydrochloride which crystallises almost completely on cooling. The addition of even 0.5 per cent. of pararosaniline to commercial rosaniline can be detected by the foregoing treatment by the separation of brown crystals after twelve hours' keeping; the presence of larger quantities, 5 to 10 per cent., can be detected by the separation of crystals immediately on cooling.

**Magenta.**—The commercial product is a mixture of the hydrochlorides of pararosaniline and rosaniline. Rosaniline hydrochloride forms more or less well-developed crystals with a cantharides lustre. It is sparingly soluble in cold water, but rather more readily in hot water; it dissolves very easily in alcohol.

Commercial magenta is graded in different brands not only according to its purity and shade, but also by its appearance and by the size of the crystals. The largest and finest crystals are usually termed Diamond Magenta.

The examination of magenta necessitates a dye trial and also an estimation of the moisture at 100°. In some cases a test for arsenic is applied. In addition to the hydrochloride, the acetate is occasionally met with; it differs from the former by its greater solubility, and usually is not crystalline.

For the volumetric analysis of magenta and new magenta by means of acid dyestuffs, see Pelet and Garuti.<sup>3</sup>

**New Magenta** (*M. L. Br.*) is produced by heating diaminoditolylmethane and *o*-toluidine hydrochloride with an oxidising agent. The commercial product is a green powder which is more easily soluble in water than ordinary magenta. In other respects it is similar to the latter.

**Acid Magenta** (Magenta S).—The dyestuff occurring in commerce under this name is generally the acid sodium salt of rosanilinesulphonic acid. Its red solution is decolorised by an excess of alkali, and is coloured yellowish brown by strong acids only at great concentrations.

It behaves like an acid dye towards animal fibres, the shade being very much like that of ordinary magenta. Acid magenta is extensively

<sup>1</sup> Knecht, *J. Soc. Dyers and Col.*, 1905, 21, 293.

<sup>2</sup> *Ber.*, 1904, 37, 3031.

<sup>3</sup> *Z. Farb. Ind.*, 1908, 7, 44.

employed in wool dyeing, and possesses the advantage over ordinary magenta that it can be mixed with other acid dyes.

**Methyl Violet** is produced by oxidising dimethylaniline (heating a mixture of dimethylaniline, phenol, sodium chloride, and copper sulphate) and consists essentially of the hydrochlorides of penta- and hexa-methylpararosaniline. It occurs in amorphous masses with a green lustre, and dissolves easily in water with a splendid violet colour, and also in alcohol. Alkalis precipitate the base from the aqueous solution in the form of a violet-brown precipitate. Alcoholic solutions are decolorised by alkalis. The dye is precipitated almost completely from its aqueous solution by sodium chloride. When an aqueous solution of methyl violet is treated gradually with a strong mineral acid, it acquires at first a blue and then a green colour, and finally, in the presence of a large excess, the colour disappears, leaving a dirty brown mixture. On dilution with water, the colour changes are exhibited in the reversed order. Reducing agents convert methyl violet into a leuco base, which is moderately stable in air.

Methyl violet is one of the most important dyes. Apart from the benzylated violets and crystal violet (see below), various bluer and redder brands are brought on the market. The latter of these are mainly products obtained from a mixture of mono- and di-methylaniline.

Like rosaniline, methyl violet is a basic dye which fixes directly on wool, silk, and leather, whilst cotton requires mordanting with tannin. Acids and acid salts retard the development of the colour on the fibre.

**Benzyl Violet.**—Violet dyestuffs occur in commerce, which in general show a behaviour very similar to that of methyl violet, but differ from it in giving much bluer shades. Such dyestuffs are obtained by treating the base of methyl violet with benzyl chloride.

**Crystal Violet** is prepared by the action of carbonyl chloride on dimethylaniline in the presence of zinc chloride.

Two kinds are brought on the market. **Crystal Violet 5BO**, forms crystals with a cantharides lustre, or hydrated ( $8H_2O$ ) crystals (yellow) with a bronze lustre, which are obtained by drying at the ordinary temperature.

It resembles methyl violet in its behaviour. (For Analysis, see Knecht.<sup>1</sup>)

**Ethyl Violet**, obtained from diethylaniline and carbonyl chloride, is a green crystalline powder, which produces a bluer colour than the preceding.

**Hofmann's Violet** (Iodine Violet), and Violet 4RN are dyestuffs which are obtained by the action of methyl iodide or methyl chloride, or ethylating agents on rosaniline, and are employed only to a small

<sup>1</sup> *J. Soc. Dyers and Col.*, 1905, 21, 293. •

extent. The same is true of the products resulting from the action of methyl chloride and ethyl bromide on Methyl Violet, which were rather more extensively used formerly under the names **Methyl Green** or **Ethyl Green**. By treatment with fuming sulphuric acid, alkylated rosanilines, such as Violet 4RN, etc., are converted into acid dyes, which find a limited application under the names **Red Violet 5RS, 4RS, Violet 4RSN, etc.** They dye silk in pure, reddish violet shades. The sulphonic acids of benzyl violet also occur commercially under the name "**Acid Violet.**" **Acid Violet 4BN** (*B.A.S.F.; Soc. Chem. Ind., Basle*) is prepared by warming tetramethyldiaminobenzophenone and benzylmethylaniline with phosphoryl chloride and sulphonating the resulting benzylpentamethylpararosaniline. Wool and silk are dyed bluish violet in an acid bath.

The commercial product is a blue powder which dissolves in water with a bluish violet colour. Hydrochloric acid produces at first a blue precipitate; the colour is changed to green on dilution, and a blue solution is the final result. Sodium hydroxide produces a blue flocculent precipitate; a colourless solution is obtained on warming. The dye dissolves in concentrated sulphuric acid with a yellow colour, which becomes olive, then green, and finally blue on dilution with water.

**Formyl Violet** (*Geigy; Cassella*) is obtained by treating benzylethyl-anilinesulphonic acid with formaldehyde, and subsequently oxidising the product together with 1 mol. of diethylaniline. Its behaviour with reagents is like that of the preceding dye.

**Acid Violet 6BN** (*B.A.S.F.; Soc. Chem. Ind., Basle*) is prepared by condensing Michler's ketone with *m*-ethoxyphenyl-*p*-tolylamine and sulphonating the product. The commercial product is a dark violet powder which dissolves in water with a bluish violet colour. The solution becomes redder in the presence of hydrochloric acid, and is decolorised by sodium hydroxide. Concentrated sulphuric acid produces an orange-red solution, which becomes reddish violet and then bluish violet on dilution.

It dyes wool and silk violet-blue from an acid bath.

**Acid Violet 7B** (*B.A.S.F.; Soc. Chem. Ind., Basle*) is obtained by treating the chloride of *p*-diethylaminobenzoic acid with methyldiphenylamine and sulphonating the product.

It dyes wool and silk bluish violet in an acid bath. The dyestuff is a violet powder which dissolves in water with a bluish violet colour. Hydrochloric acid produces a green solution. Sodium hydroxide gives a blue precipitate; the solution is decolorised on warming.

The dye forms an orange-red solution in concentrated sulphuric acid, which becomes violet on dilution.

**Alkali Violet** (*B.A.S.F.; Soc. Chem. Ind., Basle*).—Tetraethyldiaminobenzophenone is condensed with methyldiphenylamine, and the

product is sulphonated and converted into the sodium salt. The latter is a bluish violet powder which dissolves in water with a bluish violet colour. The aqueous solution gives a blue precipitate with hydrochloric acid; an excess of the acid produces a yellowish red solution. Sodium hydroxide precipitates blue flocks. Concentrated sulphuric acid produces a yellowish red solution, which becomes turbid on dilution with water owing to the formation of a dirty green precipitate.

In an acid, neutral, or alkaline bath, wool is dyed in bluish violet shades which are moderately fast to milling.

**Alkali Violet R** and **4B** also belong to this class.

**Fast Acid Violet 10B** (*Bayer*) is prepared by treating tetramethyldiaminobenzhydrol with benzylethylanilinedisulphonic acid and oxidising the product.

It is a grey powder which dissolves in water with a reddish violet colour. Sodium hydroxide does not cause any change, whilst hydrochloric acid forms a citron-yellow solution. Concentrated sulphuric acid produces an orange-yellow solution. Wool is dyed violet-blue in an acid-bath.

**Acid Violet 6B** (*Akt. Ges.*) is prepared by oxidising the product obtained by condensing dimethyl-*p*-aminobenzaldehyde with benzylethylanilinesulphonic acid. It dyes wool bluish violet from an acid bath. The commercial product is a bluish violet powder which gives a bluish violet solution in water. The solution in hydrochloric acid is bluish green, and in sodium hydroxide pale blue to colourless. Concentrated sulphuric acid produces a brownish yellow solution, which becomes darker on dilution and finally bluish green.

**Fast Wool Blue** (*Geigy*) is the acid sodium salt of tetramethylethylbenzylpararosanilinetrisulphonic acid, and dyes wool blue from an acid bath. It is a dark blue powder which dissolves in water with a blue colour. Hydrochloric acid produces a blue precipitate and then a green solution. Sodium hydroxide does not cause any change. Sulphuric acid produces a brownish yellow solution which becomes green on dilution.

**Höchst New Blue** is prepared by sulphonating the product obtained by the action of carbonyl chloride on methyldiphenylamine. Wool is dyed blue in an acid bath. The commercial product is a dark blue powder which dissolves in water with a blue colour. The solution yields a precipitate with hydrochloric acid, and is decolorised by sodium hydroxide. Concentrated sulphuric acid produces a brownish red solution.

**Eriocyanine** (*Geigy*) is the sodium salt of the anhydride of dibenzyltetramethylpararosanilinedisulphonic acid.

In the presence of sodium sulphate and sulphuric acid wool is dyed in blue shades which are fast to alkali.

**Aniline Blue** (Diphenylrosaniline<sup>1</sup>) is the basis of a series of very important blue dyestuffs. Sometimes it is employed in the form of the hydrochloride or acetate, but generally in the form of its various sulphonic acids.

The commercial products are classified under the following main groups:—

Spirit blue . . (Diphenylrosaniline ; Hydrochloride or acetate).

Alkali blue . . (Diphenylrosanilinesulphonic acid).

Water blue . . (Diphenylrosanilinedi-, tri-, or tetrasulphonic acid).

**Spirit Blue.**—Pure diphenylrosaniline hydrochloride forms small, crystalline needles with a green lustre, which are insoluble in water, but dissolve sparingly in alcohol and rather more easily in hot aniline and glacial acetic acid. The colour of the solutions is a pure greenish blue.

The base from which the salt is derived is colourless and dissolves easily in alcohol, less readily in ether. The solutions have a faint red colour. The hydrochloride is precipitated from the alcoholic solution by hydrochloric acid.

The acetate is rather more soluble in alcohol than the hydrochloride.

Different brands are brought on the market which give colours varying from pure greenish blue to violet.

When silk and wool are to be dyed, an alcoholic solution of the dyestuff is added little by little to the bath strongly acidified with sulphuric acid. Cotton must be previously mordanted by treating it first with a strong soap solution and then with aluminium acetate. The dyeing is then performed in the same way but in a neutral bath.

The dye is prepared by heating rosaniline base with an excess of aniline in the presence of benzoic acid.

The blue prepared from pararosaniline (triphenylpararosaniline) is characterised by a very pure greenish shade. Like ordinary diphenylrosaniline it is rarely employed as such, but serves chiefly for the preparation of the sulphonic acids described below.

**Alkali Blue.**—Diphenylrosanilinesulphonic acid, or rather its salts, play a very important part in the dyeing industry under the name Alkali Blue. Diphenylrosanilinesulphonic acid is a blue powder which is sparingly soluble in water. The alkali salts dissolve in water with a faint greyish blue colour. They possess the important property of being fixed on wool and silk in an alkaline solution. The colour is developed completely in an acid or "reviving" bath.

Alkali blue is employed chiefly in wool dyeing. The process of dyeing is as follows:—The wool or silk is steeped in a bath to which borax (about 15 per cent. of the material to be dyed) is added. The

<sup>1</sup> Baeyer and Williger, *Ber.*, 1904, 37, 2870 ; Lambrecht, *ibid.*, 1907, 40, 247.

dye solution is added and the material is dyed in the water-bath until the dye-bath has been almost decolorised. The operation requires one to two hours. The fabric is then removed, washed with water, and placed in a reviving bath containing about 1 per cent. of sulphuric acid. The faint greyish blue colour of the fabric acquires its full blue shade in the acid bath.

*Preparation.*—Alkali blue is obtained by carefully treating diphenylrosaniline with concentrated sulphuric acid. The sulphonic acid is precipitated by water, thoroughly washed, and converted into the sodium salt by evaporation with sodium hydroxide. Dyes producing greenish or reddish shades are obtained according to the quality of the spirit blue used in the preparation.

**Water Blue.**—The term Water Blue comprises the more easily soluble polysulphonic acids of diphenylrosaniline. They differ from alkali blue in that the free acids are easily soluble in water. Moreover a distinction is drawn between the reddish and the greenish commercial marks, Water Blue for Silk and Water Blue for Cotton. The former is a mixture of the di- with some tri-sulphonic acid. It is precipitated from its aqueous solution by acid and sodium chloride, differing in this respect from Water Blue for Cotton, which consists of the tri- together with the tetra-sulphonic acid.

Water blue is seldom employed in wool dyeing, since it is distinctly inferior to alkali blue in fastness to washing.

Silk is dyed with water blue in the presence of a little sulphuric acid. Cotton is treated first with a strong soap solution and then with alum, and is finally dyed in a faintly acid bath.

*Preparation.*—Water blue is obtained by the more prolonged and energetic treatment of spirit blue with concentrated sulphuric acid. Since the easily soluble sulphonic acids are only partially precipitated by water from the sulphuric acid solution, the latter is generally neutralised by lime, whereby the sparingly soluble calcium sulphate is precipitated and the calcium salts of the sulphonic acids remain in the solution, from which they are isolated by evaporation.

**Helvetia Blue** (*Geigy*) is the sodium salt of triphenylpararosaniline-trisulphonic acid. It is prepared by condensing 2 mol. of diphenylamine-sulphonic acid with 1 mol. of formaldehyde, and oxidising the resulting methanedisulphonic acid with another molecule of diphenylamine-sulphonic acid.

### 3. Diphenylnaphthylmethane Dyes.

**Victoria Blue B**, which is closely related to the rosaniline dyes, is prepared by the action of phenyl- $\alpha$ -naphthylamine on tetramethyldiaminobenzophenone. It dyes wool, silk, and tannin-mordanted cotton a beautiful pure blue shade. The commercial product is a

violet-black or glistening bronzy powder, which dissolves in hot water and in alcohol with a deep blue colour. Hydrochloric acid produces a precipitate which dissolves after the addition of more acid, forming a brown solution. Sodium hydroxide produces a brown precipitate. The reddish brown solution in concentrated sulphuric acid becomes yellow, then olive-green, and finally blue, on dilution with water.

**Victoria Blue, 4R**, which behaves similarly, is obtained from tetramethyldiaminobenzophenone and phenylmethyl- $\alpha$ -naphthylamine. It produces a redder colour than the brand B.

**Night Blue** is produced from tetraethyldiaminobenzophenone and *p*-tolyl- $\alpha$ -naphthylamine. The commercial product is the phosphate. It produces on silk bright greenish blue shades which do not alter their appearance in artificial light.

**New Victoria Blue (Bayer), Victoria Blue R (B.A.S.F.; Soc. Chem. Ind., Basle)** is formed by the action of Michler's ketone on ethyl- $\alpha$ -naphthylamine, and dyes in rather redder shades than does Victoria blue B.

**Acid Blue R (Sandoz)** is a blue powder which dissolves in water with a blue colour. Hydrochloric acid produces a blue precipitate which dissolves on further addition of the acid, forming a grey to reddish brown solution. Sodium hydroxide does not affect the cold solution, which, however, becomes pale blue on boiling. The reddish brown solution in concentrated sulphuric acid becomes bluish green on dilution with water. Acid blue R is dyed in the presence of 10 per cent. of sodium sulphate and 2 per cent. of concentrated sulphuric acid, and produces thus on wool a beautiful medium blue which in stronger shades may be used as a dark navy blue. The dyeings are very fast to alkali and to milling. The dyestuff is also employed as a groundwork for logwood black.

**Acid Blue B (Sandoz).**—The commercial product is a blue powder. The aqueous solution is blue and gives with hydrochloric acid a blue precipitate which dissolves in the presence of more acid with a green or reddish brown colour. The aqueous solution is not changed by sodium hydroxide in the cold, but becomes violet on heating. The reddish brown solution in concentrated sulphuric acid acquires a bluish green colour on dilution.

The dye is employed like acid blue R, but produces a greener and rather brighter blue.

**Acid Violet 5BS (Sandoz)** is a dark violet powder which dissolves in water with a violet colour. The aqueous solution yields with hydrochloric acid a violet precipitate, which is dissolved by the addition of more acid with a dirty green and finally yellowish brown colour. Sodium hydroxide does not change the aqueous solution in the cold; on warming, a reddish violet colour is developed. Concentrated

sulphuric acid produces a yellowish brown solution which becomes bluish violet on dilution.

The dye is employed like acid blue R. It produces on wool a violet colour which is fast to alkali and is rather redder than that developed by the following dye.

**Acid Violet 6BNS** (*Sandoz*) is a violet powder which dissolves in water with a violet colour. The violet precipitate, which is produced in the aqueous solution by hydrochloric acid, dissolves on the addition of more acid with a green and then yellowish brown colour. By the addition of sodium hydroxide the aqueous solution becomes blue, and on warming pale blue. The yellowish brown solution in concentrated sulphuric acid becomes green on dilution and then blue.

The dye is employed like acid blue R. It dyes wool the same shade as does Acid Violet 6BN (*B.A.S.F.*). The colours are fast to alkali and to milling.

**Acid Violet 7BS** (*Sandoz*) is a violet powder. The violet aqueous solution yields with concentrated hydrochloric acid a violet precipitate, which dissolves in more of the acid with a green and then yellowish brown colour. Sodium hydroxide produces in the cold a blue precipitate, and in the hot solution a pale blue coloration. The yellowish brown solution in concentrated sulphuric acid becomes green and then blue on dilution.

The dye is employed like acid blue R and dyes wool a very pure bluish violet colour of the shade produced by Acid Violet 7B (*B.A.S.F.*); the colours, however, are fast to alkali.

**Wool Green S** is prepared by the condensation of tetramethyldiaminobenzophenone chloride with  $\beta$ -naphthol and subsequent sulphonation. The commercial product is a brown powder which dissolves in water with a greenish blue colour. Hydrochloric acid produces a yellowish brown solution; sodium hydroxide changes the colour to reddish. Concentrated sulphuric acid produces a violet-brown solution which becomes yellowish green by dilution.

**Chrome Blue** (*Bayer*) is brought on the market as a black paste, and is prepared by the condensation of tetramethyldiaminobenzhydrol with  $\alpha$ -hydroxynaphthoic acid and oxidation of the product. Chromed wool is dyed blue.

**Naphthalene Green V.** (and Naphthalene Green concentrated<sup>1</sup>) is prepared by condensing naphthalenedisulphonic acid with tetramethyldiaminobenzhydrol and oxidising the resulting leuco compound. It is a dark red powder, which is sparingly soluble in cold water and dissolves easily in hot water. The solution yields a dark green precipitate with sodium hydroxide and is turned orange-yellow by hydrochloric acid. Stannous chloride and hydrochloric acid change

<sup>1</sup> *Rev. Gen. Mat. Col.*, 1899, 3, 198.



the green colour of the solution to yellow without decolorising it even at the boiling point. Concentrated sulphuric acid produces an orange-yellow solution which becomes rather greener on dilution with water. The dye dissolves slightly in alcohol with a green colour. In an acid bath wool is dyed rather bluer than by acid green. It is faster to alkali than acid green.

**Brilliant Milling Green B** (*Cassella*)<sup>1</sup> is a bluish green powder which dissolves in water with the same colour. The aqueous solution gives a brownish yellow precipitate with hydrochloric acid, and a pale orange precipitate with sodium hydroxide. Concentrated sulphuric acid produces a brownish yellow solution from which a yellowish-green precipitate is obtained on dilution with water.

#### 4. Rosolic Acid Dyes.

**Yellow Corallin.**—The product denoted by this name is not a chemical individual. Pararosolic acid,  $C_{19}H_{14}O_3$ , although not the chief constituent, is that which has been most thoroughly examined. In addition to this acid, there are also present its homologues, as well as a large number of other compounds, for example, rosolic acid itself, which give shades very similar to that of pararosolic acid.

In the pure state, rosolic acid and pararosolic acid both form red crystals with a blue reflex, are insoluble in water, and dissolve moderately easily in alcohol, ether, and concentrated hydrochloric acid; the solutions are golden yellow. They combine with sodium hydrogen sulphite to form colourless compounds. Reducing agents convert them into the corresponding leuco-rosolic acids. The rosolic acids combine with alkalis to form salts which have a splendid red colour and are soluble in water.

**Aurin** (as sodium salt) forms orange-yellow masses with a green lustre, which dissolve in water with a fine red colour.

It is prepared by heating a mixture of phenol, oxalic acid, and sulphuric acid.

**Red Corallin** (Peonin) is the commercial name of a product which is obtained by heating aurin with ammonium hydroxide under pressure. Probably a partial replacement of hydroxyl by amino-groups occurs. The product exhibits a much redder shade than aurin, which it otherwise resembles. Acids give a red precipitate with the alkaline solution. Aurin and red corallin are employed only to a very slight extent in dyeing. They cannot be fixed either on wool or silk. Cotton can be dyed by red corallin in a similar way as by eosin with the addition of lead acetate, but the colour is of a very fugitive character.

<sup>1</sup> *Rev. Gen. Mat. Col.*, 1900, 4, 8.

Rosolic acid dyes form very fine lakes with metallic salts, which are fairly extensively employed in the paper industry. Frequently paper is dyed by merely soaking it in an alkaline solution of the dyestuff.

**Chrome Violet** (*Geigy; Bayer*) is the sodium salt of aurintricarboxylic acid, and is produced by warming a mixture of salicylic acid, concentrated sulphuric acid, methyl alcohol, and sodium nitrite. The dye is fixed by means of chromium mordants and produces a violet colour. It is employed chiefly in calico printing.

The commercial product is a brown powder which dissolves in water with a brownish red colour.

Sodium hydroxide produces a pale brown solution, whilst hydrochloric acid precipitates the free acid. The latter is also obtained when the brown solution of the dye in concentrated sulphuric acid is diluted with water.

### 5. Phthaleins.

**Fluorescein, Resorcinolphthalein,  $C_{20}H_{12}O_5$** .—According to the solvent from which it has been separated, pure fluorescein is a yellowish red powder, or consists of more or less well-developed crystals of a pale yellow to dark red colour. It cannot be melted or volatilised without decomposition, but withstands a temperature of  $280^\circ$ ; above this, however, it decomposes, turns brown, and finally carbonises. It is almost insoluble in water, but dissolves moderately readily in alcohol and ether, still more easily in glacial acetic acid. These solutions exhibit generally only a slight fluorescence. Fluorescein possesses a pronounced acid character and forms salts with alkalis, which are easily soluble in water, and exhibit a magnificent green fluorescence even in very dilute solutions.

Fluorescein is an important intermediate product in the preparation of many dyestuffs derived from phthalic acid, and is occasionally employed as a yellow dye; for this purpose it is brought on the market in the form of an alkali salt, under the name Uranin. Fluorescein dyes wool and silk in an acid bath, and produces a greenish yellow colour, which unfortunately shows very little fastness to light and air. The quality of a commercial product is determined by the purity of the colour but, above all, by the quality of the eosin produced from it.

*Preparation.*—One molecule of phthalic acid is mixed with 2 mol. of resorcinol, and the mixture is heated at  $190$  to  $200^\circ$  until it has solidified completely and no longer evolves steam.

Chlorinated fluoresceins are prepared from chlorinated phthalic acids (especially tetrachlorophthalic acid), and are employed in the production of dyestuffs which are brought on the market under the names, Phloxin, Cyanosin, and Rose Bengal. These products are

obtained in an analogous manner to fluorescein, but differ from it in their much feebler fluorescence.

**Chrysolin** is prepared by heating a mixture of resorcinol, phthalic anhydride, benzyl chloride, and sulphuric acid. It dyes silk and wool yellow.

**Eosin** is the sodium or potassium derivative of tetrabromo-fluorescein. In the pure state, the free acid consists of a reddish yellow powder or of more or less well-developed yellowish red crystals. It is very slightly soluble in water, and is rather more easily soluble in alcohol and glacial acetic acid, but not in benzene. It separates from alcoholic solution in crystals containing alcohol of crystallisation. It is a moderately strong dibasic acid, and forms salts with alkalis, which dissolve easily in water with a fine red colour.

Solutions of free eosin do not fluoresce, whilst those of its salts exhibit a strong yellow fluorescence. The disappearance of the fluorescence by acidification is accompanied by a precipitation of the dyestuff if the solution is sufficiently concentrated.

The commercial product is usually the sodium salt. This consists of a red powder which is very easily soluble in water, but more sparingly so in alcohol. From aqueous solutions of eosin salts, finely coloured lakes are precipitated by metallic salts; for example, by salts of lead, tin, zinc, and aluminium. Eosin is decolorised by sodium amalgam; when the resulting solution is rendered alkaline and treated with potassium chromate, the green fluorescence of fluorescein is regenerated. If zinc dust is used, the decolorised solution yields eosin on oxidation.

Eosin is one of the most brilliant red dyestuffs. On wool and silk it produces a yellowish shade which is very characteristic. When cotton is being dyed, a little lead acetate is added to the bath. The resulting lead lake then gradually fixes itself on the material. Yellowish and bluish eosins are brought on the market; they differ from each other chiefly in their bromine content. As a rule, the more yellowish shades are produced by the dyes containing less bromine. Eosin is prepared by brominating fluorescein in alcoholic solution. It can be estimated with titanous chloride.<sup>1</sup>

**Spirit Eosin, Primrose, Eosin BB** (Methyl- or Ethyl-eosin).—The monoalkyl ethers of eosin, which still contain a hydroxyl group, behave like monobasic acids. Their salts are almost insoluble in water, and are only slightly soluble in absolute alcohol, but dissolve easily in 50 per cent. alcohol.

The commercial product is generally the sodium or the potassium salt. Spirit eosin differs from eosins which are soluble in water, in producing a bluer shade which gives magnificent effects, particularly

<sup>1</sup> Knecht, *J. Soc. Dyers and Col.*, 1905, 21, 294.

on silk. The concentrated solution of spirit eosin is yellowish red, and becomes rose coloured on dilution, showing a splendid yellowish green fluorescence. Like ordinary eosin, it forms finely coloured lakes with most metallic salts.

**Dibromodinitrofluorescein** (Safrosin, Nopalin, Eosin Scarlet).—The dyestuff is a strong acid which separates in yellow needles from alcohol and glacial acetic acid, in which it is only sparingly soluble. The salts are easily soluble in water, producing a yellowish red or a rose colour in concentrated or dilute solution respectively. The solutions do not fluoresce, and this dye is thus sharply distinguished from the eosins. In ammoniacal solution, the dye is decolorised by zinc dust; the solution, however, acquires a bluish red colour owing to atmospheric oxidation. The commercial product is generally the sodium salt.

The dyestuff exhibits a bluer shade than the eosins and is distinguished from these by its greater colour intensity. It is employed chiefly on wool, less frequently on silk and cotton. Before the discovery of the azo dyes, it was employed, mixed with yellow dyestuffs (particularly dinitronaphthol), for the production of scarlet-red shades. Dibromodinitrofluorescein is prepared by treating fluorescein successively with nitric acid and with bromine, or by the action of nitric acid on eosin.

**Tetraiodofluorescein** (Erythrosin, Eosin J) is very similar to eosin in its chemical properties, but differs from it, however, in its much bluer shade and also in the absence of fluorescence. It is very easily detected by heating it in a test tube with sulphuric acid, whereby the violet vapour of iodine is evolved. It produces a very fine rose colour, especially on silk; its application is confined almost entirely to dyeing silk and paper.

**Phloxin, Cyanosin, Rose Bengal.**—These substances bear the same relation to the di- and tetra-chlorofluoresceins prepared from chlorinated phthalic acids as eosin, spirit eosin, and erythrosin do to ordinary fluorescein. Phloxin is the bromine derivative, and rose Bengal the iodine derivative of these chlorinated fluoresceins. Their solutions do not fluoresce, although this property becomes apparent on silk dyed by them. Cyanosin is the ethyl ether of phloxin and, analogously to the eosin ethers, is soluble only in dilute alcohol.

In comparison with the non-chlorinated eosins, these derivatives are characterised by their bluer shades. They are numbered amongst the finest red dyestuffs and are employed almost exclusively in silk dyeing. (For analysis, cf. Jean., *Rev. Gen. Mat. Col.*, 1908, 12, 2.)

**Rhodamine B** (*B.A.S.F.*; *Soc. Chem. Ind., Basle*; *M. L. Br.*) can be regarded as fluorescein, in which two hydroxyl groups are replaced by two ethylated amino-groups.

It is obtained by heating diethyl-*m*-aminophenol with phthalic anhydride or by the interaction of diethylamine and fluorescein chloride.

Rhodamine possesses basic properties owing to the presence of the substituted amino-groups. It dyes silk, wool, and tannin-mordanted cotton a bluish red shade which surpasses the eosin colours in beauty. Rhodamine is moderately fast to light.

The commercial product is a red powder which dissolves in water and in alcohol with a red colour. Dilute solutions exhibit a strong fluorescence. At the ordinary temperature sodium hydroxide does not cause any change; by heating, red flocks are produced and the odour of diethylamine becomes appreciable. An excess of hydrochloric acid produces a yellowish red solution which acquires a violet tinge on dilution. It dissolves in concentrated sulphuric acid (with the evolution of hydrochloric acid), forming a brownish yellow solution which becomes yellowish red and then bluish red on dilution with water.

Its analysis can be carried out with titanous chloride.<sup>1</sup>

Quite similar, and differing only in the shade, are **Rhodamine 3B** (the ethyl ester of the preceding dye), **Rhodamine G** (consisting chiefly of triethylrhodamine), and **Rhodamine 6G** (the ethyl ester of *s*-diethylrhodamine).

**Rhodamine S** is prepared by heating succinic anhydride with dimethyl-*m*-aminophenol. The commercial product dissolves in water with a red colour and a yellow fluorescence. The solution is decolorised by sodium hydroxide.

It is employed in dyeing cotton in place of safflower carmine. The unmordanted fibre is dyed a very fine rose-red in an acetic acid bath.

**Fast Acid Eosin G** (*M. L. Br.*)<sup>2</sup> is a red powder which dissolves easily in water with a greenish yellow fluorescence. The solution becomes strongly reddish yellow and the fluorescence is diminished in the presence of sodium hydroxide. Hydrochloric acid is without action. Concentrated sulphuric acid produces a pale yellow solution.

In the presence of 10 per cent. of sodium sulphate and 4 per cent. of sulphuric acid, wool is dyed in very pure, fluorescent rose shades. The fastness to light is better than that of the rhodamine 6G colours.

Similar dyestuffs are Fast Acid Phloxin A, Cotton Rhodine BS, Irisamine.

The Violamines or Fast Acid Violets also belong to this class. They are obtained by heating fluorescein chloride with aniline (and similar amines) and subsequently sulphonating the product, or by the

<sup>1</sup> Knecht, *J. Soc. Dyers and Col.*, 1905, 21, 294.

<sup>2</sup> *Rev. Gen. Mat. Col.*, 1899, 3, 90.

condensation of *m*-hydroxydiphenylamine (and its analogues) with phthalic anhydride.

**Violamine B** or **Fast Acid Violet B** (*M. L. Br.*) is a dark violet powder which dissolves in water with a violet colour. The solution yields a blue flocculent precipitate with hydrochloric acid, and is unchanged by sodium hydroxide. Sulphuric acid produces a yellowish red solution which gives a blue precipitate on dilution.

It dyes silk and wool in violet shades which are moderately fast to light and milling.

Similar dyestuffs are Violamine R, Violamine G (Acid Rosamine A), Violamine 2 R (Fast Acid Blue R).

**Gallein** and **Coerulein**. — Gallein is produced by heating gallic acid with phthalic anhydride. It is a brown powder which is insoluble in water, and dissolves in alkalis with a red colour which becomes blue in presence of excess of the alkali.

Gallein, as such, is of little importance in dyeing; it constitutes, however, the material from which is produced Coerulein, a dye of great importance in calico printing.

Coerulein is obtained by heating gallein and concentrated sulphuric acid at about 200°. It is a blue-black powder which is insoluble in water, alcohol, and ether. It is slightly soluble in glacial acetic acid with a green colour. It forms a colourless soluble compound with sodium hydrogen sulphite. This property and the fact that it forms lakes with chromium oxide and alumina account for its application in dyeing.

The bisulphite compound, mixed with chromium acetate, is printed on the material, which is then steamed. By this procedure the bisulphite compound is decomposed and the chromium oxide lake is produced. In this way coerulein develops a dark green colour which is very fast to soaping and to light.

Coerulein is also employed extensively for dyeing chromed wool.

The commercial products are: Coerulein Paste, a black paste, and Coerulein S, a powder or a paste (the bisulphite compound).

## VI. HYDROXYQUINONES AND QUINONEOXIMES.

### 1. Anthracene Dyes.

Dyestuffs derived from anthracene, of which alizarin is the most important representative, constitute a class which is sharply distinguished from other coal tar dyes, not only in respect of their preparation, but also in their application. The anthracene dyestuffs are chiefly employed in calico printing and in cotton dyeing; but their consumption in wool dyeing has attained large dimensions in recent

years. They produce shades which (with the exception of Turkey Red) are usually not so bright as those given by other coal-tar dyes, but possess the advantage of great stability.

**Alizarin** (Dihydroxyanthraquinone),  $C_{14}H_8O_2$ . Pure alizarin forms reddish brown needles. It melts at  $289-290^\circ$ , and at higher temperatures sublimes in red needles. It is almost insoluble in cold water and dissolves very sparingly in hot water. It is also sparingly soluble in cold alcohol, rather more easily in boiling alcohol, and dissolves fairly readily in glacial acetic acid, methyl alcohol, acetone, or glycerol. All these solutions have a yellowish red colour. Concentrated sulphuric acid has no action on alizarin even at  $150-200^\circ$ . Alizarin is insoluble in a boiling solution of alum.

It behaves towards alkalis like a weak dibasic acid. The alkali salts are easily soluble in water, the primary salts with a red, and the secondary salts with a purple-violet colour. The former are produced by dissolving alizarin in solutions of carbonates or other alkaline salts, the latter are formed in an excess of the alkali hydroxides. The heavy metals and the metals of the alkaline earths form usually sparingly soluble lakes which are distinguished by more or less characteristic colours. These lakes are produced by precipitating a solution of the alkali derivative by the metallic salt in question, and also by the direct combination of alizarin with the metallic oxide. The analysis of alizarin dyestuffs by the application of this property can be effected by Dreaper's method.<sup>1</sup>

The different colours of the alizarin lakes are of great importance in the dyeing industry; by their means very diverse shades, varying from a fiery red to a deep blackish violet can be obtained.

Alizarin is fixed on fabrics entirely in the form of its lakes, of which those of aluminium, chromium, and iron are of chief importance.

Artificial alizarin is brought on the market usually in the form of a paste. The amount of alizarin varies between 20 and 60 per cent., according to circumstances, but a 20 per cent. paste is the commonest form.

The consistence of the paste gives no indication of the amount of alizarin. A quite neutral article is thin; viscous pastes, such as are preferred by many consumers, contain a trace of free acid. For export, a 100 per cent. alizarin is manufactured; this is either converted into a 20 per cent. paste by solution in sodium hydroxide and reprecipitation by an acid or in the form of an alkaline solution is introduced directly into the dye-bath, where it is precipitated by a suitable acid.

Alizarin mixed with starch is also placed on the market in the solid form. Other methods are also adopted for producing the dry material or a material containing a large percentage of the dyestuff.<sup>2</sup>

<sup>1</sup> *J. Soc. Chem. Ind.*, 1893, 12, 977.

<sup>2</sup> Gnehm, *Anthracenfarbstoffe*, 1897, p. 33.

Pure alizarin, so-called Blue Shade Alizarin (Alizarin VI., etc.) dyes cotton bluish red when it is mordanted with alumina, and pure violet when an iron mordant is used.

Other substances, in addition to alizarin are present in the commercial product: Anthrapurpurin, Flavopurpurin, and also non-dyeing compounds such as hydroxyanthraquinone, anthraflavic acid, isanthraflavic acid, etc.

A dye-trial is usually considered sufficient for testing alizarin; a more thorough examination is necessary for an accurate estimation.

*Estimation of the Residue after Drying.*—About 20 g. of the paste under examination are heated in a weighed platinum dish in an air-bath at 100—110° until the weight is constant. The percentage of ash is determined by igniting the residue. To detect hydroxyanthraquinone (and anthraflavic or isanthraflavic acid), a portion is dissolved in sodium hydroxide and the hot solution is treated with a solution of barium chloride and filtered. The filtrate is treated with a solution of sodium carbonate at the boiling point, filtered again, allowed to cool, and acidified with hydrochloric acid. Hydroxyanthraquinone or anthraflavic acid or isanthraflavic acid separates in yellow flocks.

For the laboratory dye tests it is best to use calico printed with mordants. Calico, suitably prepared for this purpose, is placed on the market; it is printed with different mordants in equally broad, parallel strips. The mordants are usually pure alumina and pure iron mordants and a mixture of both. One of these pieces of calico is cut into halves across the strips and the two halves are quantitatively dyed with the sample and standard colour respectively. In some cases the dye-trial is more suitably performed on strips or skeins mordanted for Turkey-Red.

In this way some knowledge can be obtained of the behaviour of the sample under examination in the "reviving" bath.

*Preparation.*—Artificial alizarin is prepared by heating anthraquinonemonosulphonic acid and sodium hydroxide in the presence of an oxidising agent (potassium chlorate or nitrate). The alizarin precipitated from the alkaline solution by hydrochloric acid, is carefully washed and brought on the market in the form of a paste.

**Anthrapurpurin** (*iso*Purpurin), 1:2:7-Trihydroxyanthraquinone crystallises in anhydrous, orange needles, which are easily soluble in alcohol or glacial acetic acid and sparingly soluble in ether. It melts above 330°. The alkaline solution is rather redder than that of alizarine. It differs from purpurin in that it is less soluble in a boiling solution of alum. With aluminium mordants it produces a yellower red than alizarin, whilst the iron lake yields a greyish violet of little value.

Pure anthrapurpurin is put on the market as Alizarin SX and



SSA (*Brit. Alizarine Co.*), GD, RX, Sx extra, Sx, RT, and WG (for wool).

**Flavopurpurin**, 1:2:6-Trihydroxyanthraquinone. — Pure flavopurpurin crystallises in anhydrous yellow needles, which are almost insoluble in water, but dissolve easily in cold alcohol and also in glacial acetic acid. Its melting point is above  $330^{\circ}$ .

The solution in alkalis is redder than that of isopurpurin; by dilution with water it becomes dirty yellowish red. It dissolves in sodium carbonate with a yellowish red colour. With alumina mordants it produces a very yellowish red, and with iron mordants a reddish violet.

Pure flavopurpurin is put on the market as Alizarin YCA and GB (*Brit. Alizarine Co.*), GI, RG, SDG, X, No. 10, FA, and Alizarin Red WGG (for wool).

Alizarin, anthrapurpurine and flavopurpurin can be distinguished by the different colours of their alkaline solutions. With aluminium mordants alizarin produces the "bluest" red, the finest "rose" and "violet." Anthrapurpurin yields yellower shades than alizarin, although not so yellow as those produced by flavopurpurin. Flavopurpurin gives the yellowest shades; the colours of the last, however, are more appreciably affected in a reviving bath.

The following process is recommended by Perkin<sup>1</sup> for the estimation of an alizarin paste:—

Five grams of the paste (20 per cent.) are dissolved in distilled water and the solution is made up to 1 litre. Five c.c. of the solution are mixed with 5 c.c. of 2 per cent. potassium carbonate, diluted to 500 c.c., and the colour is examined.

In this way, with a little practice, it is easily possible to detect even very slight differences of shade; for example, that produced by the addition of 3 to 5 per cent. of anthrapurpurin to alizarin.

The composition of a paste can also be ascertained to a certain extent by the fact that solutions of mixtures of alizarin and anthrapurpurin are clear and pale, whilst those of alizarin and flavopurpurin are considerably darker.

Among the commercial products occur many mixtures of these three hydroxyanthraquinones in various proportions.

All of these products are tested by the process described under Alizarin.

Flavopurpurin and isopurpurin are obtained by fusion of the two isomeric anthraquinonedisulphonic acids, the former from the  $\alpha$ -acid, the latter from the  $\beta$ -acid. Both are common constituents of artificial alizarin.

**Purpurin** (1:2:4-Trihydroxyanthraquinone). — Purpurin crystal-

<sup>1</sup> *J. Soc. Chem. Ind.*, 1894, 13, 496.

lises from aqueous alcohol in long, yellow needles, which contain 1 mol. of water of crystallisation, and become red and anhydrous at  $100^{\circ}$ . It sublimes at about  $150^{\circ}$  in red feathery needles, and melts at  $253^{\circ}$ . It is much more soluble than alizarin in boiling water, and also in alcohol and ether. The solution in alkalis is red, appearing purple in thin layers. A dilute alkaline solution is very quickly bleached in air and light. With lime and baryta it forms lakes which are quite insoluble in hot water. A boiling solution of alum dissolves a considerable amount of purpurin, forming a yellowish red, strongly fluorescent solution, from which a precipitate separates on cooling, consisting of free purpurin and the aluminium lake.

An insoluble rose-red lake is produced when a solution of purpurin in sodium carbonate is treated with an insufficient quantity of alum. With aluminium mordants purpurin gives scarlet to dark red shades, which become particularly bright on soaping.

Artificial purpurin is obtained by oxidising alizarin with manganese dioxide or arsenic acid and sulphuric acid, and is placed on the market in the form of a 20 per cent. paste under the name "Alizarin No. 6," or Purpurin.

It finds little application on account of its slight fastness to light and its high price, and because the same shade can be produced by the more readily available and faster isopurpurin.

In the form of its dark chromium lake it is employed in calico printing.

**Anthragallol** (1 : 2 : 3-Trihydroxyanthraquinone).—This substance is produced by the action of benzoic acid on gallic acid in the presence of a dehydrating agent.

Anthragallol is fixed on chromed fabrics with a deep brown colour, and is fairly extensively employed in wool dyeing under the names "Anthracene Brown" or "Alizarin Brown." It comes on the market as a dark brown paste.

Anthragallol dissolves in concentrated sulphuric acid and in alkalis with a brown colour.

**Alizarin Orange** ( $\beta$ -Nitroalizarin).— $\beta$ -Nitroalizarin forms yellowish needles or leaflets melting at  $244^{\circ}$ . It sublimes in yellow leaflets, at the same time partly carbonising.

With regard to its solubility in water, alcohol, glacial acetic acid, etc., it behaves very much like alizarin. Its salts dissolve in water with a purple-red colour, but are precipitated by an excess of alkali. Nitroalizarin forms brown lakes with lime and baryta. It produces a reddish orange colour with aluminium mordants, and a reddish violet with iron mordants. It constitutes the chief ingredient of the brownish yellow pastes which are brought on the market under the names, Alizarin Orange AO (*Brit. Alizarine Co.*), Alizarin Orange A, D, Alizarin OR, OG, etc.

*Preparation.* —  $\beta$ -Nitroalizarin is prepared by the nitration of alizarin borate or by the action of nitrous acid on alizarin, which, for this purpose, is suspended in glacial acetic acid or nitrobenzene, or is spread out in thin layers on a flat surface.

**Alizarin Orange G**,  $\beta$ -Nitroflavopurpurin (*M. L. Br.*), is similar to the preceding dye.

**Alizarin Maroon** (*B.A.S.F.*) is a dark reddish brown 20 per cent. paste, consisting probably of a mixture of various aminoalizarins and aminopurpurin. It dissolves in sodium hydroxide with a violet colour. It produces Bordeaux shades with aluminium mordants, and dark brown shades with chromium mordants.

**Alizarin Claret** (*Brit. Alizarine Co.*), **Alizarin Garnet R** (*M. L. Br.*), and **Alizarin Cardinal** (*Bayer*) are reddish brown pastes consisting of  $\alpha$ -aminoalizarin. The aluminium lake is violet red; the chromium lake steel blue.

**Alizarin Red S powder** (*Brit. Alizarine Co.*), **Alizarin WS**, is the sodium salt of alizarinmonosulphonic acid; the commercial product is an orange powder which dissolves in water and in alcohol with a reddish yellow colour. The solution becomes paler in the presence of hydrochloric acid, and is turned violet by sodium hydroxide. Concentrated sulphuric acid produces a yellowish red solution. It is suitable for dyeing mordanted wool. The aluminium lake is bright scarlet red; the chromium, iron, and tin lakes produce brown, violet, and orange-yellow colours respectively.

Similar dyestuffs are Alizarin 2S (the sodium salt of anthrapurpurinmonosulphonic acid) and Alizarin 3S (the sodium salt of flavopurpurinmonosulphonic acid), which produce more yellowish shades.

**Alizarin Bordeaux B** (*Bayer*) is a tetrahydroxyanthraquinone, and is prepared by treating alizarin with fuming sulphuric acid, and subsequently hydrolysing the initially formed tetrahydroxyanthraquinone sulphate. The commercial product is a brownish red paste which dissolves in sodium hydroxide with a reddish violet colour. It is employed in cotton and wool dyeing. The aluminium lakes are Bordeaux-red, the chromium lakes violet-blue and very fast to light, soaping, and acids.

Allied compounds are put on the market under the names Bordeaux "G," "BD," "GG," "GD," and "GDD," and are employed in wool-dyeing with a chromium mordant.

**Alizarin Cyanin R** (*Bayer*) is prepared by oxidising alizarin Bordeaux, dissolved in sulphuric acid, by manganese dioxide, and treating the product with a dilute acid. In this way pentahydroxyanthraquinone is obtained.

The commercial product is a dark brown paste which is insoluble

in water, but dissolves in sodium hydroxide with a blue colour. Hydrochloric acid precipitates the dyestuff from the alkaline solution as a dark blue mass. The lakes produced on chromed wool are very similar to those of alizarin blue.

**Alizarin Cyanin G** (*Bayer*) is obtained by treating with ammonium hydroxide the intermediate substance formed in the preparation of Alizarin Pentacyanin R. - The commercial product is a black paste, which is insoluble in water but dissolves in sodium hydroxide or ammonium hydroxide with a bluish green colour. The dyestuff dissolves in concentrated sulphuric acid with a red colour. Chromed wool is dyed in greenish blue shades. The colours are characterised by great fastness to light and to alkalis. :

Other brands of Alizarin Cyanin brought on the market are: 2R, 3R, RA, RA extra, 3RA, RG, G, G extra, GG, WRR, WRB, GS extra, 3RS, RS, R extra, RR, P.

**Alizarin Viridin** in paste (*Bayer*) forms a green chromium lake. It is particularly suitable for printing both oiled and ordinary cotton. It is a sulphonated Quinizarin Green. Closely related to it is Anthraquinone Green GX (*B.A.S.F.*)<sup>1</sup>

**Alizarin Cyanin Green** (*Bayer*),<sup>2</sup> a dyestuff of similar constitution, is put on the market as a black paste, which contains sodium chloride and is slightly soluble in water and in alcohol with a green colour. The colour of the aqueous solution is unchanged by hydrochloric acid or sodium hydroxide. By the addition of an excess of acid a precipitate is formed and the liquid becomes yellowish green. The dry dyestuff freed from sodium chloride, is a dark blue-black powder, which dissolves in concentrated sulphuric acid with a violet colour; on the addition of water the solution becomes green and the dyestuff is precipitated.

It can be dyed on wool in an acid bath or by means of chromium mordants.

**Alizarin Cyanin Green G extra** and **E** are also brought on the market in the form of powders.<sup>3</sup>

**Alizarin Cyanin Black G** (*Bayer*) is a dark brown paste which is insoluble in water. By treatment with dilute hydrochloric acid a violet-red solution is produced; an excess of the acid precipitates orange-red flocks. A blackish flocculent precipitate is obtained by the addition of sodium hydroxide to the solution in hydrochloric acid. Concentrated sulphuric acid dissolves the dry dyestuff with a violet colour; on dilution with water orange-red flocks are precipitated.

With chromium mordants the dye yields a black, which is very fast to light and to milling. It is probably the sulphonic acid of the toluidide of purpurin.

<sup>1</sup> Friedlaender and Schick, *Z. Farb. Chem.*, 1904, 3, 220. <sup>2</sup> *Rev. Gen. Mat. Col.*, 1897, 1, 81.

<sup>3</sup> Friedlaender and Schick, *Z. Farb. Ind.*, 1903, 2, 439.

Alizarin Blue Black is a similar dyestuff.

**Alizarin Sky Blue** is the monosulphonic acid of 1-amino-4-*p*-toluidino-2-bromoanthraquinone.<sup>1</sup>

**Alizarin Saphirol** is probably prepared from 1:5-dinitroanthraquinone, and is a diaminoanthrachrysonedisulphonic acid. It dyes wool in an acid bath in the presence of sodium sulphate.

**Alizarin Irisol R** (*Bayer*) is 1-hydroxy-4-sulphotoluidinoanthraquinone, and is placed on the market both as a powder and a paste; it produces level dyeing in an acid bath. It develops clear bluish violet shades on wool, which are changed to bluish green by chromium salts.

**Alizarin Astrol B** (*Bayer*) is 1-methylamino-4-sulphotoluidinoanthraquinone, and produces very level dyeing, the colour being remarkably fast to light. It produces a greener shade than alizarin saphirol.

**Anthracene Blue WR** (*B.A.S.F.*) consists of hexahydroxyanthraquinone and is obtained by the action of fuming sulphuric acid on 1:5-dinitroanthraquinone. The commercial product is a blackish brown paste which is insoluble in water but dissolves in sodium hydroxide with a blue colour. The dry dyestuff forms a brownish violet, fluorescent solution in concentrated sulphuric acid. Chromed wool is dyed a reddish blue.

Similar dyestuffs are Anthracene Blue WG (which produces a greenish blue), Anthracene Blue WB (which dyes sky blue), Anthracene WRR, and Anthracene Dark Blue W.

The following brands are soluble in water: Anthracene Blue SWG (greenish blue), SWB (sky blue), and SWR (reddish blue).

**Brilliant Alizarin Cyanin R** (*Bayer*) probably also belongs to the same class.

**Acid Alizarin Blue BB and GR** (*M. L. Br.*), the sodium salts of hexahydroxyanthraquinonedisulphonic acid, are produced by boiling diaminoanthrachrysonedisulphonic acid with alkalis, and dye wool red from an acid bath. The colours become blue on subsequent treatment with chromium fluoride. The commercial product (a powder) dissolves in water with a red colour. The solution is changed to bluish violet by sodium hydroxide, and the dyestuff is precipitated by an excess of the alkali. The aqueous solution is unchanged by hydrochloric acid. Concentrated sulphuric acid produces a reddish blue solution.

**Acid Alizarin Green B and G** (*M. L. Br.*), the sodium salt of disulphohydroanthrachrysonedisulphonic acid, is obtained by reducing dinitroanthrachrysonedisulphonic acid in alkaline solution by sodium sulphide. It dyes wool greenish blue from an acid bath; by subsequent treatment with chromium fluoride or potassium bichromate, a green is produced which does not alter in artificial light.

<sup>1</sup> Friedlaender and Schick, *Z. Farb. Ind.*, 1904, 3, 220.

The dyestuffs are reddish or greenish black powders forming bluish green aqueous solutions which are turned violet by sodium hydroxide and redder by hydrochloric acid. Concentrated sulphuric acid produces blue or red solutions which become violet on dilution.

**Alizarin Blue ABT** (*Brit. Alizarine Co.*); **Alizarin Blue (B.A.S.F.)**, Dihydroxyanthraquinonequinoline; **Alizarin Blue BSS** (sodium salt: *Brit. Alizarine Co.*).

Pure alizarin blue crystallises in brown needles with a coppery lustre, melting at  $270^{\circ}$ , and can be sublimed with partial decomposition. It is insoluble in water and only slightly soluble in alcohol, but dissolves easily in amyl alcohol and glacial acetic acid. It behaves as a weak acid and also as a weak base. It forms a blue solution in alkali, provided the latter is not in excess. An excess of the alkali produces a green flocculent precipitate of the corresponding salt. It dissolves in strong acids, forming salts which are decomposed by water. In an alkaline solution it is reduced by zinc dust, forming a soluble derivative which is applicable in vat-dyeing.

With sodium hydrogen sulphite alizarin blue forms a compound which is soluble in water; the dye is now used almost entirely in the form of this compound, which is brought on the market under the name **Alizarin Blue ABS** (*Brit. Alizarine Co.*), **Alizarin Blue S**. It is a brown crystalline powder which dissolves easily in water with a reddish colour.

Alizarin blue is chiefly employed in dyeing chromed wool; it is also applied in printing, for which purpose the bisulphite compound, Alizarin Blue ABS, is most frequently used.

This compound together with chromium acetate is printed on the fabric, on which the metallic lake, produced by steaming, is fixed. The shade is an indigo-blue.

*Preparation.*—Alizarin blue is prepared by heating at about  $150^{\circ}$  a mixture of  $\beta$ -nitroalizarin (or  $\beta$ -aminoalizarin and nitrobenzene), glycerol, and sulphuric acid.

**Alizarin Green S** (*M. L. Br.*) is the bisulphite compound of  $\alpha$ -alizarinquinoline and is produced from  $\alpha$ -aminoalizarin by a process similar to the preceding. The commercial product is either a violet-blue paste or a dark powder; it dissolves in water with a violet-red colour, but is insoluble in alcohol. Sodium hydroxide produces a red solution. The red solution in concentrated sulphuric acid yields bluish green flocks of the dyestuff on dilution with water. With chromium, and particularly with nickel mordants, it forms green lakes of considerable fastness.

**Alizarin Green S in paste** (*B.A.S.F.*)—*Preparation.*—"Alizarin Blue Green," produced by the action of fuming sulphuric acid on alizarin blue, is warmed with ordinary sulphuric acid, whereby a mixture is obtained consisting of tri- and tetra-hydroxyanthraquinone

quinolines and their sulphonic acids. The commercial product, which is a yellowish brown liquid, contains the bisulphite compound. When heated alone, or, better, with hydrochloric acid, the double compound is decomposed and alizarin green is produced. The commercial product forms a violet solution in sodium hydroxide. It produces bluish green lakes with chromium mordants.

**Alizarin Green SW**, as a paste and a powder, is prepared specially for wool dyeing and printing.

**Alizarin Indigo Blue S** (*B.A.S.F.*) is prepared in a similar way. The commercial product is the sodium hydrogen sulphite compound of Alizarin Indigo Blue, and consists of a dark yellowish red liquid; which yields alizarin indigo blue on boiling. Sodium hydroxide produces a blue solution. The chromium lake is indigo-blue. The marks **Alizarin Indigo Blue SW** and **SMW** are particularly adapted for wool dyeing.

**Alizarin Black P** (*M. L. Br.*) is flavopurpurinquinoline, and is obtained from  $\beta$ -nitroflavopurpurin by a process similar to the preparation of alizarin blue. The commercial product is a greenish black paste, which is sparingly soluble in alcohol and insoluble in water. Sodium hydroxide produces a dirty green solution. The dyestuff is used in cotton printing and wool dyeing. The chromium lake is grey to black.

**Alizarin Black S** (*M. L. Br.*) is the bisulphite compound of the brand P. It is a brown solution which becomes blackish violet on the addition of sodium hydroxide. Hydrochloric acid produces a black precipitate. The dyestuff is employed in printing.

**Indanthren S** (*Scholl*)<sup>1</sup> (*B.A.S.F.*) is obtained by heating  $\beta$ -aminoanthraquinone with potassium hydroxide at 250° (*R. Bohn*), and is *N*-dihydro-1:2:2':1'-anthraquinoneazine. It possesses a feeble basic character, and represents the first true real vat dye of the anthracene series.

It is insoluble in most organic solvents, and dissolves best in boiling quinoline.

With sodium hyposulphite and sodium hydroxide it forms immediately a blue vat, from which cotton directly absorbs the dyestuff without greening.

**Indanthren C** (*B.A.S.F.*) is a mixture of di- and tri-bromoindanthren, and is obtained by the direct action of bromine on indanthren. The colours are very fast to chlorine and are greener than those of brand S. It is not to be recommended for printing. The commercial product is a greyish blue paste.

**Flavanthren** is prepared by heating  $\beta$ -aminoanthraquinone with potassium hydroxide to 330°—350° in the presence of air, or to 270° in

<sup>1</sup> *Ber.*, 1903, 36, 3426.

presence of potassium nitrate. It gives a violet-blue vat, and dyes the same colour, which is, however, rapidly changed to yellow by atmospheric oxidation. The brand R is more highly purified and redder than the brand G.

**Indanthren CD** is dichloroindanthren. It is suitable only for calico printing.

**Melanthren B** is prepared by an analogous method to indanthren, a diaminoanthraquinone being substituted for the monoamino-derivative. It is a greyish paste and gives a brown vat; the dyeings are grey.

**Fuscanthren** is obtained by submitting the formaldehyde compounds of certain diaminoanthraquinones to the same reaction. It is a reddish brown dyestuff and gives a yellowish brown vat.

**Cyananthren B double** is prepared by melting benzanthrone-quinoline with alkali hydroxides.

**Violanthren** is similarly obtained from benzanthrone.<sup>1</sup>

**Cibanone Black G and R, Cibanone Yellow R, Cibanone Orange R, Cibanone Brown B and V**, are anthraquinone vat dyes containing sulphur.

## 2. Naphthalene Dyes.

**Naphthazarin** (Dihydroxynaphthaquinone) is prepared by heating dinitronaphthalene with a solution of sulphur sesquioxide (a solution of sulphur in fuming sulphuric acid). The commercial product, **Alizarin Black S, SW, SRW, WR, Naphthazarin S, Alizarin Blue Black RW**, is the bisulphite compound of the dihydroxynaphthaquinone thereby produced. The commercial article is a brown paste (or a dark powder). It is insoluble in cold water, but dissolves in hot water with a brown colour. It dissolves in alcohol with a yellowish brown colour and greenish yellow fluorescence, in sodium hydroxide with a fine blue colour, and in hydrochloric acid with a brownish red colour. The dirty yellowish brown solution in concentrated sulphuric acid evolves sulphur dioxide on heating, becomes red, and gives a black precipitate on dilution. The chromium lake is black, and is characterised by great fastness to light, air, milling, and acids.

**Alizarin Black SRA** is the bisulphite compound of an anilide of naphthazarin.

**Alizarin Black WX (B.A.S.F.)** is tetrahydroxynaphthalene.

**Alizarin Dark Green (B.A.S.F.)** is produced in the naphthazarin fusion in the presence of phenols. \*

**Fast Black B (B.A.S.F.)** is prepared by treating 1:8-dinitronaphthalene with an aqueous solution of sodium sulphide. The commercial product is a blackish blue paste which is insoluble in water and alcohol, and forms a violet solution by warming with sodium hydroxide. Unmordanted cotton is dyed a fast black in an alkaline bath.

<sup>1</sup> Brown, *J. Soc. Dyers and Col.*, 1906, 22, 11.\*



**Fast Black BS** (*B.A.S.F.*) is the product of the action of alkalis on fast black B. It is brought on the market as a bluish black paste which dissolves in water with a violet-blue colour. The dyestuff is precipitated from the solution by acids. The dry dyestuff dissolves in concentrated sulphuric acid with a dirty green colour, and in alcohol with a violet-blue colour.

Cotton and silk are dyed black even in the cold.

### 3. Quinoneoximes.

**Dinitrosoresorcinol** (Dioximinoquinone).—The dinitrosoresorcinol produced by the action of nitrous acid on resorcinol, possesses the property of forming iron lakes of a dark green shade, and therefore is employed in calico printing and in dyeing. It is placed on the market in the form of a paste, under the names "Fast Green O," "Chlorin," "Dark Green," "Alsace Green," etc.

Pure dinitrosoresorcinol is almost colourless and is slightly soluble in water; it dissolves in alkalis with a faint yellow colour. It produces a very dark green precipitate in a solution of ferrous sulphate, especially in the presence of sodium acetate. It forms a pale yellow solution in hydrochloric acid. Cotton or wool, treated with iron mordants, are dyed in a bath faintly acidified with acetic acid.

**Gambin G, Y, Steam Green S**, is the product of the action of nitrous acid on  $\beta$ -naphthol ( $\beta$ -naphthaquinoneoxime), and similarly forms green lakes with iron mordants. It is an olive green paste, which is sparingly soluble in water, but dissolves in alkalis with a yellow colour and a greenish yellow fluorescence.

Similar dyestuffs are **Gambin R** ( $\alpha$ -Naphthaquinoneoxime), and **Gambin B** or **Dioxin** (prepared from 2:7-dihydroxynaphthalene and nitrous acid).

The iron salt of the last-mentioned dyestuff is probably present in **Milling Green S** (*Leonhardt*), which dyes wool without a mordant. **Naphthol Green B** (*Cassella*) is the ferrous sodium salt of nitroso- $\beta$ -naphthol-6-sulphonic acid. The commercial product is a dark green powder, which dissolves in water with a pale green colour. The solution is unchanged by hydrochloric acid, and is coloured bluish green by sodium hydroxide. Concentrated sulphuric acid produces a brownish yellow solution. Wool is dyed green from an acid bath.

## VII. QUINONEIMIDE DYES.

### I. Thiazines.

**Methylene Blue**.—The zinc chloride double salt, which is the chief constituent of the commercial product, crystallises from dilute alcohol in fine prisms with a coppery lustre. It is also easily soluble in water

and is precipitated from the solution by sodium chloride, especially in the presence of an excess of zinc chloride.

The colour of methylene blue in solution is a pure greenish blue, which is not changed by dilute acids or by ammonium hydroxide. Dilute sodium hydroxide produces a blue precipitate, whilst more concentrated solutions produce a faintly reddish violet precipitate. The dyestuff dissolves in concentrated sulphuric acid with a yellowish green colour, and in concentrated hydrochloric acid with a faint bluish green colour. The original blue colour is regenerated by the addition of water. Reducing agents, such as ammonium sulphide, or hydrochloric acid and zinc dust, rapidly decolorise the blue solution. The colour is reproduced, slowly in the air, instantly, when an oxidising agent (ferric chloride, potassium bichromate) is added to the acidified solution. This behaviour furnishes a means of detecting the dyestuff, especially on the fibre. Ammonium sulphide produces at once on the material a white spot which, after being treated with an acid, becomes blue again, slowly of itself, instantly when moistened with a drop of ferric chloride.

Methylene blue is a very valuable dyestuff which plays an important part, particularly in cotton dyeing and printing. It produces beautiful greenish blue shades directly on wool and silk. On tannin-mordanted cotton it produces rather a dull indigo shade.

It is prepared by oxidising dimethyl-*p*-phenylenediamine in the presence of dimethylaniline and sodium thiosulphate.

L. Pelet and V. Garuti<sup>1</sup> estimate methylene blue volumetrically by titrating a 0.1 to 0.2 per cent. solution of the dye with an equally dilute solution of a suitable acid dye of as different a colour as possible. The end-point is ascertained by "spotting." Crystal ponceau gives the best results. Carmine (the sodium salt), pyramine orange, or cotton brown, can also be used. Methylene blue combines with crystal ponceau in the proportion of 2 mol. of the blue to 1 mol. of ponceau, and with carmine in the proportion 1 : 1. (The principle on which this process is based has already been employed by Rawson and Knecht<sup>2</sup> for a similar purpose.) Knecht<sup>3</sup> estimates methylene blue by titrating its solution in hydrochloric acid, with titanous chloride, in an atmosphere of carbon dioxide, until the colour disappears, and obtains a sharp end-point and accurate results.

The following dyestuffs behave towards reagents in a similar manner:—

**Gentianine** (*Geigy*) is a mixture of methylene blue and Lauth's violet, and dyes tannin-mordanted cotton bluish violet.

**Ethylene Blue** (*Oehler*), **Thionine Blue** (*M. L. Br.*), **Toluidine Blue** and **New Methylene Blue W** (*Cassella*), also belong to this class.

<sup>1</sup> *Bull. Soc. Chim.*, 1904, [iii.], 31, 1094; *Z. Farb. Ind.*, 1908, 7, 44.

<sup>2</sup> *J. Soc. Dyers and Col.*, 1888, 4, 84.

<sup>3</sup> *Ibid.*, 1905, 21, 9.

**Thiocarmine R** (*Cassella*) is the sodium salt of dibenzyl-diethylthioninedisulphonic acid. The dyestuff is brought on the market as a blue powder or a paste. It dissolves in water with a blue colour. The solution is not changed by hydrochloric acid, but becomes violet on warming with sodium hydroxide. Concentrated sulphuric acid produces a green solution, which becomes blue on dilution with water. Animal fibres are dyed indigo-blue from an acid bath; the colours, however, are sensitive to light.

**Indochromogen S** (*Sandoz*), a sulphoxyindophenolthiosulphonic acid of the naphthalene series, is a dark blue powder, which dissolves in water with a reddish violet colour. Hydrochloric acid produces a yellowish brown solution; sodium hydroxide produces a dirty violet solution, which becomes blue on boiling, owing to the formation of a thiazine. The solution in concentrated sulphuric acid is greenish yellow, and becomes reddish violet on dilution.

Cotton, previously treated with alkaline turkey-red oil, is printed with indochromogen S, and a chromium or a mixed chromium-calcium mordant; by subsequent steaming, very bright blue chromium lakes of the thiazine dyestuffs are produced, such as cannot be obtained by direct printing of the thiazines themselves. Fabrics treated with indochromogen S and chromium-calcium acetate can be readily discharged by potassium ferrocyanide and potassium chlorate or colour printed.

**Indochromine T** (*Sandoz*), **Brilliant Alizarin Blue** (*Bayer*), is a mordant thiazine dye of the naphthalene series.

The commercial product is a dark powder with a bronze lustre or a paste consisting of lustrous bronze needles. It dissolves in water with a sky-blue colour; the solution gives a blue precipitate with hydrochloric acid. An excess of sodium hydroxide produces a blue precipitate. The yellowish green solution in concentrated sulphuric acid gives a violet precipitate on dilution.

With chromium mordants, it forms beautiful greenish blue colours in a bath slightly acidified with acetic acid; the colours on wool are especially characterised by their very great fastness to milling and to light.

The dyestuff is also employed with chromium acetate on oiled fabrics in cotton printing, but the shades are not so bright as those produced by indochromogen S.

**Methylene Green** (*M. L. Br.*) is mononitromethylene blue. It is prepared by treating methylene blue in an acid solution with nitrous acid.

The commercial product is a dark brown powder which dissolves in water with a greenish blue colour. The solution is rendered greener by hydrochloric acid. Sodium hydroxide precipitates violet flocks.

The green solution in concentrated sulphuric acid becomes blue on dilution with water.

## 2. Oxazines and Oxazones.

**Capri Blue GN** (*Leonhardt*)<sup>1</sup> is obtained by treating nitrosodimethylaniline hydrochloride with diethyl-*m*-aminocresol.<sup>1</sup> The commercial product, consisting of small glistening green crystals, is the zinc chloride double salt. It dissolves in water and in alcohol with a blue colour. The solution is reddened by hydrochloric acid, whilst sodium hydroxide produces a violet precipitate. The green solution in concentrated sulphuric acid becomes red on dilution with water. The dyestuff produces a very greenish blue on silk and tannin-mordanted cotton.

Closely related to it are **Cresyl Blue BB** and **Cresyl Violet B** and **BB** of the same firm.

**Brilliant Cresyl Blue 2B** (*Leonhardt*)<sup>2</sup> is prepared from nitrosodimethyl-*m*-aminocresol and benzyl-*m*-aminodimethyl-*p*-toluidine, and is soluble in cold water and in alcohol with a blue colour. Hydrochloric acid produces a brownish yellow precipitate, and sodium hydroxide a yellowish red precipitate. The yellowish green solution in concentrated sulphuric acid becomes brownish yellow and then blue on dilution. The aqueous solution is instantly decolorised by stannous chloride and hydrochloric acid.

It can be employed for dyeing tannin-mordanted cotton and silk, and gives very pure blue shades.

**Meldola's Blue** (Naphthol Blue, New Blue, Fast Blue).—This dyestuff, discovered by Meldola and prepared by the action of nitrosodimethylaniline hydrochloride on  $\beta$ -naphthol, has found special application in cotton dyeing. The commercial product (the zinc chloride double salt) is a brown, crystalline powder, the dust of which attacks the mucous membrane very strongly. It dissolves easily in water with a bluish violet colour, and in concentrated sulphuric acid with a greenish blue colour.

It produces on tannin-mordanted cotton a grey-blue with a violet tinge, which is moderately fast to light and to soaping, but is not fast to alkali.

**Muscarine** (*Durana*) is prepared by the action of nitrosodimethylaniline hydrochloride on 2:7-dihydroxynaphthalene.

The commercial product is a brownish violet powder, which is sparingly soluble in cold water but dissolves easily in hot water with a bluish violet colour. The aqueous solution gives a violet-blue precipitate with hydrochloric acid. Sodium hydroxide forms a

<sup>1</sup> Möhlau, Klimmer, and Kahl, *Z. Farb. Ind.*, 1902, 1, 313.

<sup>2</sup> *Rev. Gen. Mat. Col.*, 1899, 3, 56.

brownish yellow solution. Concentrated sulphuric acid produces a bluish green solution from which violet flocks are precipitated by water.

Tannin-mordanted cotton is dyed blue.

**Nile Blue A** (*B.A.S.F.*) is prepared by the interaction of nitroso-diethyl-*m*-aminophenol hydrochloride and  $\alpha$ -naphthylamine.

The commercial product is a lustrous bronze powder which dissolves in warm water and in alcohol with a blue colour. From the warm solution the hydrochloride is precipitated, in crystalline needles, by the addition of hydrochloric acid. The aqueous solution gives a red precipitate with dilute sodium hydroxide; by shaking with ether, it acquires an orange colour and a green fluorescence. Concentrated sulphuric acid produces a green solution which becomes green, and finally blue on dilution.

Tannin-mordanted cotton and silk are dyed blue.

Similar colours are produced by **Nile Blue 2B** (prepared from nitrosodiethyl-*m*-aminophenol hydrochloride and benzyl- $\alpha$ -naphthylamine) and **Nile Blue R**.

**New Methylene Blue GG** (*Cassella*) is prepared by the action of dimethylamine on Meldola's blue and subsequent oxidation.

It is a grey powder which dissolves in water with a blue colour. An excess of hydrochloric acid produces a brown colour, whilst sodium hydroxide produces a blackish blue precipitate. The brown solution in concentrated sulphuric acid becomes blue on dilution with water. Tannin-mordanted cotton is dyed greenish blue.

**Metamine Blue B** is an analogous dyestuff, prepared from Meldola's blue and dimethyl-*p*-phenylenediamine.

**Fluorescent Blue** is obtained by brominating resorufin. The commercial product is a 10 per cent. olive-brown liquid containing small green crystals (the ammonium salt). It dissolves in boiling water, giving a violet solution which is strongly fluorescent. The solution gives a brown precipitate with hydrochloric acid, but is not changed by sodium hydroxide. The dry dyestuff dissolves in concentrated sulphuric acid with a blue colour, and is reprecipitated from the solution by water. In an acid bath silk and wool are dyed in greyish blue shades with a reddish brown fluorescence.

**Alizarin Green G** (*Dahl*) is prepared by the condensation of an alkaline solution of  $\beta$ -naphthaquinonesulphonic acid with 1-amino-2-naphthol-6-sulphonic acid.

The commercial product is a brownish black powder which dissolves in hot water with a green colour. The solution is reddened by hydrochloric acid and gives a red precipitate. Sodium hydroxide also produces a precipitate. The bluish green solution in concentrated sulphuric acid gives a red precipitate on dilution.

It dyes green on chromium mordants.

**Alizarin Green B** is derived from 2-amino-1-naphthol-4-sulphonic acid.

**Gallocyanine** (Fast Violet).—This dyestuff is prepared by the action of nitrosodimethylaniline hydrochloride on gallic acid. It is employed in calico printing and in wool dyeing, and is fixed on the fibre in the form of its chromium lake.

Gallocyanine is brought on the market in the form of a powder or a paste. It is only slightly soluble in water and in alcohol. It possesses the properties of a weak acid and also of a weak base. It is sparingly soluble in hydrochloric acid with a reddish colour, and easily forms a violet solution in alkali hydroxides or carbonates, from which it is precipitated by acetic acid. Concentrated sulphuric acid produces a blue solution. With chromium oxide mordants gallocyanine produces a beautiful bluish violet colour, which is very stable.

**Gallocyanine BS** is the bisulphite compound of gallocyanine.

**Brilliant Gallocyanine** (*Durand, Huguenin & Co.*) produces brighter and bluer dyeings, and is more easily soluble.

**Violet Moderne N**, of the same firm, is obtained by removing the carboxyl group of gallocyanine, and the "**Bleus modernes**" are prepared by treating the gallocyanines with formaldehyde.

**Gallocyanine S** (*Durand, Huguenin & Co.*) is a gallocyanine-sulphonic acid.

**Prune** (*Sandoz*) is prepared by the action of nitrosodimethylaniline hydrochloride on methyl gallate. The commercial product occurs as a dark brown powder or a paste. The dyestuff differs from gallocyanine by its ready solubility in water. The solution is reddened by hydrochloric acid. Sodium hydroxide produces first a precipitate, and then a violet solution. The blue solution in concentrated sulphuric acid becomes red on dilution with water.

It dyes chromed wool and cotton bluish violet; it can also be fixed on cotton by means of tannin.

**Delphine Blue** (*Sandoz*) is obtained by sulphonating the anilide produced by treating gallocyanine with aniline.

The dyestuff is placed on the market as a dark paste (the free sulphonic acid) or as a brown powder (the ammonium salt). The latter dissolves in water, the former in ammonium hydroxide or dilute sodium hydroxide, with violet-blue colours. The solution becomes magenta-red by the addition of hydrochloric acid, and yields a dark flocculent precipitate. Sodium hydroxide produces a dirty violet precipitate which is soluble in water. The reddish violet solution in concentrated sulphuric acid becomes red on dilution and a flocculent blue precipitate is produced.

It dyes wool in an acid bath. It is usually dyed, however, on chromium mordants, forming in this case greenish blue lakes.

Similar dyestuffs are the **Chromazurines** (*Durand, Huguenin & Co.*).

**Gallamine Blue** (*Geigy*) is obtained by the action of nitrosodimethylaniline hydrochloride on gallamic acid. The commercial product is a greenish grey paste, which dissolves sparingly in boiling water with a greenish blue colour. The solution in hydrochloric acid is red, and in sodium hydroxide violet. Concentrated sulphuric acid produces a red solution which appears green in thin layers; it remains red when diluted with water.

Chromed wool is dyed bluish violet (as in the case of gallocyanine).

**Correine RR** (*Durand, Huguenin & Co.*), **Celestine Blue B** (*Bayer*), is prepared by the interaction of gallamide and the hydrochloride of diethylaminoazobenzene or of nitrosodiethylaniline.

It is a greenish black powder, which dissolves in water with a violet-blue colour. The solution is reddened by hydrochloric acid. The solution in sodium hydroxide is bluish violet. Concentrated sulphuric acid produces a blue solution which becomes red on dilution. With chromium mordants the dyestuff yields reddish blue lakes.

**Correine AR** results by the action of aniline on correine and sulphonation of the product.

Similar substances (gallanilide derivatives) occur in **Gallanil Indigo P** and **Gallanil Indigo PS**.

**Phenocyanine** (*Durand, Huguenin & Co.*),<sup>1</sup> obtained by the action of resorcinol on ethylgallocyanine, is a yellowish green paste, which is insoluble in water and in alcohol, but dissolves in sodium hydroxide with a brown colour.

Concentrated sulphuric acid produces a brown solution, which gradually turns blue.

The dyestuff is especially suitable for printing.

**Gallazine A** (*Durand, Huguenin & Co.*) is produced by oxidising the substance obtained by treating gallocyanine with  $\beta$ -naphthol-6-sulphonic acid S.

The commercial product is a brown paste, which is almost insoluble in water and alcohol. It dissolves in sodium hydroxide with a violet colour. Concentrated sulphuric acid produces a blue solution.

Chromed wool is dyed blue.

**Gallanil Green** (*Durand, Huguenin & Co.*).—To prepare this dyestuff, the product of the interaction of nitrosodimethylaniline and gallanilide is treated with aniline, and subsequently sulphonated and nitrated.

The commercial product is a brown paste or a powder with a bronze lustre, which dissolves in water with a bluish green colour. The solution gives a blue precipitate with hydrochloric acid. Sodium hydroxide produces a redder solution and finally a precipitate. The

<sup>1</sup> *Z. Farb. Ind.*, 1902, 1, 165.

red solution in concentrated sulphuric acid becomes turbid on dilution owing to the formation of a precipitate.

Chromed wool is dyed green.

**Indalizarin R, 2R, J, JR** (*Durand, Huguenin & Co.*)<sup>1</sup>—Brands R and 2R are greenish grey pastes; J is a greenish liquid; JR is a greenish paste.

These dyestuffs are the bisulphite compounds of gallocyanine-sulphonic acids. They are fixed by means of chromium mordants; for example, chromium acetate or chromium bisulphite.

The dyestuffs are soluble in sodium hydroxide and in sodium acetate, the solutions rapidly becoming blue on exposure to the air. In sulphuric acid brand R forms a pale brown solution, 2R a violet-brown, J a reddish brown, and JR a violet-brown; by the addition of manganese dioxide the colour becomes violet in the case of R, or bluish violet in the other cases. The solutions of all of the four brands in sulphuric acid become violet on dilution with water.

**Indalizarin Green** is a nitro-derivative of indalizarin.

**"Cyanines modernes"** (*Durand, Huguenin & Co.*) are condensation products of gallocyanines and dialkyldiamines.

**"Heliotropes modernes,"** of the same firm, are gallocyanines prepared from nitrosomonoalkylanilines, and **Leucogallothionines** are obtained by condensing alkyldiaminothiosulphonic acids with gallic acid or its derivatives.

## VIII. AZINE DYES.

### 1. Eurhodines.

**Neutral Violet** and **Neutral Red** (*Cassella*), produced by the joint oxidation of dimethyl-*p*-phenylenediamine and *m*-phenylene- or *m*-tolylenediamine, are dyestuffs which give reddish brown and violet colours on tannin-mordanted cotton. They are blackish green powders which dissolve in water with a violet-red colour. The colours become blue in the presence of hydrochloric acid; sodium hydroxide produces precipitates. The solutions in concentrated sulphuric acid are green, which become red on dilution with water.

### 2. Safranines.

**Safranine** (Safranine T; GOO⊙; G extra, etc.).—Safranine constitutes a strong base, the salts of which are fine red dyestuffs. The commercial product is usually the hydrochloride. In the pure state it consists of metallic-looking, brown, crystalline needles, which are sparingly soluble in cold water, easily in hot, and are still more readily soluble in alcohol. The colour of the concentrated solutions is yellowish

<sup>1</sup> *Rev. Gen. Mat. Col.*, 1899, 3, 250.



red, that of dilute solutions rose-red. The alcoholic solution exhibits a strong yellow-brown fluorescence, which is not seen in the aqueous solution.

Safranine is one of the few dyestuffs the bases of which are soluble in water and the salts of which are not decomposed by alkalis. Consequently an aqueous solution of safranine hydrochloride is not precipitated by dilute sodium hydroxide or potassium hydroxide; concentrated solutions of the alkalis, however, precipitate the unchanged hydrochloride. Safranine exhibits a remarkable variety of colours when treated with concentrated acids.

With concentrated hydrochloric acid it produces a magnificent blue colour, whilst a green coloration is developed with concentrated sulphuric acid. The latter changes gradually through blue and violet to red when the solution is diluted with water.

When boiled with zinc dust, the dyestuff is converted into a leuco compound, which is easily reoxidised in the air. The commercial product is a brown powder. Safranine produces a shade intermediate between those of magenta and eosin. It is employed for producing rose tones chiefly on cotton, frequently also in admixture with yellow dyestuffs, for the development of ponceau shades.

It dyes wool and silk directly from a neutral bath. It also dyes unmordanted cotton, but only to a slight extent. It is usual, therefore, to mordant the cotton with tannin and tartar emetic. Unfortunately safranine has the disadvantage of not being fast to light.

Methods of analysis have been given by Knecht<sup>1</sup> and Pelet and Garuti.<sup>2</sup>

For the preparation of safranine aminoazotoluene is reduced, for example, by iron filings and hydrochloric acid, whereby *p*-tolylenediamine and *o*-toluidine are produced; these bases, in the form of their hydrochlorides, are mixed with 1 mol. of aniline hydrochloride (or toluidine) and oxidised with sodium bichromate or manganese dioxide.

**Fuchsia, Clematine, Giroflé, Tannin Heliotrope, Amethyst Violet, and Iris Violet** are similar dyestuffs to safranine, but of much more limited application.

**Silk Grey** (*M. L. Br.*) is obtained by oxidising the product of the interaction of *as*-dimethyl- or diethyl-phenosafranine and formaldehyde. From an acid, boiled-off liquor bath, silk is dyed grey.

By the combination of diazotised safranines with  $\beta$ -naphthol, etc., valuable azo dyes have been prepared, for example:—

**Indoine R** (*B.A.S.F.*) is a dark paste or a powder which dissolves in water and in alcohol with a bluish violet colour. Hydrochloric acid produces a blue precipitate, and sodium hydroxide a dark violet

<sup>1</sup> *J. Soc. Dyers and Col.*, 1905, 21, 294.

<sup>2</sup> *Z. Farb. Ind.*, 1908, 7, 44.

precipitate. The blackish brown solution in concentrated sulphuric acid yields the dyestuff on dilution with water.

Tannin-mordanted cotton is dyed in very fast indigo shades.

It can be analysed by Knecht's method.<sup>1</sup>

**Naphthindone BB** (*Cassella*), **Diazine Blue BB**, **Diazine Black**, **Diazine Green** (*Kalle*), and **Brilliant Diazine Blue** are similar products.

Compare also the Janus dyes (p. 970).

**Mauveine**.—Free mauveine is a powder which is insoluble in water, but dissolves in alcohol with a bluish violet colour. It is a very strong base which displaces ammonia from ammonium salts and can combine with carbon dioxide. The solutions of its salts have a purple-red colour somewhat resembling that of potassium permanganate. Most of the salts crystallise well, and dissolve easily in hot water; they are less readily soluble in cold water. Mauveine and its salts produce green colours in concentrated sulphuric acid, which change through blue to violet by the addition of water. It gives a blue coloration with concentrated hydrochloric acid. On wool and silk it produces a shade intermediate between violet and Bordeaux.

Mauveine is still occasionally employed for colouring English postage stamps and for whitening silk.

For its preparation a mixture of aniline and toluidine, in the form of their salts, is oxidised by a neutral solution of potassium bichromate or other oxidising agent.

**Rosolane** (*M. L. Br.*).—A dyestuff similar to mauveine is prepared by oxidising a mixture of *p*-aminodiphenylamine, *o*-toluidine, and aniline.

**Indazine** (*Cassella*) is prepared by the interaction of nitrosodimethylaniline hydrochloride and diphenyl-*m*-phenylenediamine.

The commercial product is a powder which is easily soluble in water and in alcohol with a blue colour. Hydrochloric acid has no action. Sodium hydroxide produces a blue precipitate. The dark green solution in concentrated sulphuric acid becomes blue on dilution.

Tannin-mordanted cotton is dyed indigo-blue.

An analogous dyestuff, **Metaphenylene Blue B** (*Cassella*), is produced from di-*o*-tolyl-*m*-phenylenediamine. **Brilliant Rosinduline Red B** and **BD** (*Bayer*) are dyestuffs obtained by the action of *p*-nitrosomethyl-*o*-toluidine on *p*-monosubstituted tolylenediamines.

**Magdala Red** (Naphthalene Rose).

Naphthalene rose is the safranine of the naphthalene series. Its salts, like those of safranine, are not attacked by alkali hydroxides. On reduction, it yields a vat which instantly reoxidises in the air. It dissolves in concentrated sulphuric acid with a greenish black colour. The hydrochloride, which constitutes the ordinary form of the dyestuff, crystallises in slender brown needles, which are sparingly soluble in

<sup>1</sup> *J. Soc. Dyers and Col.*, 1905, 21, 294. •

and easily so in alcohol. On silk it produces, especially in very dyeings, a fine fluorescent rose shade. It is used to a limited extent in silk dyeing.

Naphthalene rose is obtained by heating aminoazonaphthalene and thylaminé hydrochloride in the presence of glacial acetic acid.

**Tilling Blue** (*Kille*) is prepared by fusing benzeneazo- $\alpha$ -naphthyl-amine with  $\alpha$ -naphthylamine hydrochloride and aniline, and the dyestuff is sulphonated. It is a bronze powder which dissolves in water with a blue colour. The aqueous solution gives a blue precipitate with hydrochloric acid. The solution is darkened by sodium hydroxide. The bluish green solution in concentrated sulphuric acid becomes blue on dilution.

Chromed wool is dyed blue.

**Basle Blue R** (*Durand, Huguenin & Co.*) is prepared by the reaction of nitrosodimethylaniline hydrochloride on 2:7-ditolyl-naphthyl-amine.

It is a brown powder which dissolves in water with a bluish violet colour. The aqueous solution gives a blue precipitate with hydrochloric acid.

Concentrated sulphuric acid produces a dirty green solution, from which a blue precipitate is obtained by the addition of water.

Lannin-mordanted cotton is dyed blue.

A sulphonic acid of this dyestuff is brought on the market under the name **Basle Blue S**.

This class also includes **Azo Green T** (*Leonhardt*), **Neutral Grey** (*Ges.*), **Naphthazine Blue** (*Dahl; M. L. Br.*), and **Ethyl Blue** (*L. Br.*).

### 3. Aposafranines.

**Induline Scarlet** (*A.B.S.F.*) is prepared by melting azo derivatives of monoethyl-*p*-toluidine with  $\alpha$ -naphthylamine hydrochloride.

The commercial product is a red powder, which dissolves in water with a red colour. Hydrochloric acid has no action, whilst sodium hydroxide produces a violet precipitate. The red solution in concentrated sulphuric acid becomes green, and then red on dilution.

Lannin-mordanted cotton is dyed scarlet red.

**Azo Carmine G** (*B.A.S.F.*) is obtained by sulphonating phenyl-induline. The commercial product is a red, glistening paste which dissolves sparingly in water, forming a bluish red solution. Sodium hydroxide has no action; hydrochloric acid produces a red precipitate. Concentrated sulphuric acid forms a green solution which gives a red precipitate with water. It is used as an archil substitute, producing a dyeing in bluish red shades.

Sulphonic acids of phenylrosinduline or of rosindone occur in the following dyestuffs:—

**Azo Carmine B, Rosinduline 2B, and Rosinduline 2G** (*Kalle*).

**Diphenyl Blue B and R** (*Akt. Ges.*)<sup>1</sup> are employed for printing and dyeing cotton, being fixed by tannin. Very pure colours are obtained, which are very fast to washing.

#### 4. Indulines.

**Indulines.**—By the action of aniline on azo and nitro compounds, especially on aminoazobenzene, azobenzene, azoxybenzene, and nitrobenzene, grey and greyish blue dyestuffs are produced, which have attained a certain importance. The dyestuffs are of a basic character, but combine with acids to form salts which are insoluble or only very slightly soluble in water. Consequently, for most purposes they are converted into the sulphonic acid by treatment with concentrated sulphuric acid.

The dyestuffs show the following reactions:—The unsulphonated substances are almost insoluble in water, but dissolve moderately readily in alcohol. The colour of the solution is greyish blue with a more or less red tinge. Alkalis produce a reddish violet colour in the solution. From the greenish blue solution in concentrated sulphuric acid, water precipitates the sparingly soluble sulphate when heating is prevented. The sulphonic acids as such are moderately sparingly soluble in water. They dissolve in alkalis with the reddish violet colour of the free base. From concentrated solutions the sulphonic acid is precipitated on acidification with hydrochloric acid.

The sulphonic acids of the indulines are very valuable wool dyes. They are employed in the presence of alum or sulphuric acid and sodium sulphate, and produce a greyish blue shade similar to that of indigo.

Indulines, which are soluble in alcohol, are fixed on cotton by tannin, and are somewhat extensively employed in calico printing.

They are also fixed by the so-called acetin process. The indulines, in a very finely divided state, are printed together with acetin or diacetin (acetates of glycerol) and tannin.

On steaming, the acetins dissolve the induline, but, being ultimately hydrolysed to acetic acid and glycerol, the former is driven off. Simultaneously the dissolved induline forms a lake with the tannin and becomes fixed on the fibre.

Under the name "Nigrosine," products are placed on the market which are obtained by the action of nitrobenzene and nitrophenol on aniline. They are employed in the form of sulphonic acids, and produce on wool shades which are similar to those of the indulines, but not so pure.

**Paraphenylene Blue** (*Dahl*) is produced by the action of *p*-

<sup>1</sup> *Rev. Gen. Mat. Col.*, 1899, 3, 284.

phenylenediamine on aminoazobenzene, azophenine, azobenzene, and, in general, on substances which yield indulines by similar treatment with aniline.

Paraphenylene blue, as is to be expected, is an amino-derivative of induline, and its properties confirm this assumption. It possesses a stronger basic character, and its salts are stable and are soluble in water. The aqueous solution gives a precipitate with sodium hydroxide. Concentrated sulphuric acid produces a blue solution.

It is employed chiefly in cotton dyeing and printing, and produces a very dark blackish blue with tannin mordants.

**Tolylene Blue B** (*Oehler*) is produced by the action of *p*-phenylenediamine on an induline which is soluble in alcohol. The commercial product dissolves in water with an indigo-blue colour, and dyes tannin-mordanted cotton indigo blue. An excess of hydrochloric acid or sodium hydroxide produces a precipitate in the aqueous solution. Concentrated sulphuric acid produces a blue solution. **Para Blue** (*Nötsel*), a dyestuff obtained by heating spirit blue with *p*-phenylenediamine, behaves in a similar way towards reagents.

### 5. Quinoxaline Dyes.

**Flavinduline** is obtained by the action of phenanthraquinone on *o*-aminodiphenylamine, and dissolves in water with a yellow colour. The aqueous solution gives a yellow precipitate with sodium hydroxide, and is not attacked by hydrochloric acid. Concentrated sulphuric acid produces a red solution, which becomes yellow on dilution.

Tannin-mordanted cotton is dyed yellow.

## IX. QUINOLINE DYES.

**Cyanine**, **Quinoline Red**, and **Flavaniline** are no longer employed in the textile industry. **Quinoline Yellow** (obtained by heating quinoline and phthalic anhydride in the presence of zinc chloride), which is soluble in alcohol, is of importance, and especially so is its sulphonic acid, which occurs in **Quinoline Yellow S** in the form of the sodium salt. This dyestuff dissolves in water with a yellow colour, and produces very bright greenish yellow shades on wool and silk in an acid bath.

The solution becomes rather paler in the presence of hydrochloric acid, and is darkened by sodium hydroxide. Concentrated sulphuric acid produces an orange-red solution, which becomes yellow on dilution.

## X. ACRIDINE DYES.

The reaction between meta-diamines or *as*-alkylated meta-diamines and formaldehyde yields tetra-aminodiphenylmethane or its derivatives,

from which hydroacridines are produced by the elimination of ammonia. By oxidising the latter, the corresponding acridins are obtained, many of which are brought on the market as useful yellow and orange dyestuffs.

**Acridine Yellow** (*Leonhardt*), prepared from *m*-tolylenediamine and formaldehyde as above, dyes tannin-mordanted cotton and silk yellow; the colours on silk exhibit a green fluorescence. The aqueous fluorescent solution yields yellow precipitates with hydrochloric acid and sodium hydroxide. Concentrated sulphuric acid produces a yellow solution, which becomes turbid on dilution with water.

**Acridine Orange** (from dimethyl-*m*-phenylenediamine and formaldehyde) forms an orange-yellow, strongly fluorescent solution in water. The solution is reddened by hydrochloric acid. Sodium hydroxide produces a yellow precipitate. A slightly coloured, fluorescent solution is formed in concentrated sulphuric acid, which becomes red and then orange by dilution.

Silk and tannin-mordanted cotton are dyed yellow; the colours on silk are fluorescent.

Corresponding derivatives of phenylacridine are obtained when meta-diamines are condensed with benzaldehyde instead of formaldehyde. Many of these are also used as dyestuffs.

**Benzoflavine** (*Oehler*), from benzaldehyde and *m*-tolylenediamine, dyes tannin-mordanted cotton, silk, and wool yellow, and behaves like acridine yellow towards reagents.

**Acridine Orange R extra** (*Leonhardt*), from benzaldehyde and dimethyl-*m*-phenylenediamine, resembles ordinary acridine orange in its behaviour. **Homophosphine G** (*Leonhardt*), which produces a yellower and clearer shade than the preceding brand, probably also belongs to this class.

**Phosphine** [Chrysaniline, Leather Brown, Vitoline Yellow 5G (*Ter Meer*) etc.].—The pure substance is a pale yellow powder, which is very sparingly soluble in water, but dissolves easily in alcohol. It is a pronounced base and forms easily soluble, crystalline salts, which are very fine yellow dyestuffs. The nitrate is the most sparingly soluble, and the most easily crystallisable salt.

Phosphine belongs to the series of acridine dyes. Its simplest representative,  $C_{19}H_{15}N_3$ , is *as*-diaminophenylacridine. Like all these substances, it is very stable towards chemical reagents. Amongst its other properties, the base can be distilled partly undecomposed. It dissolves in concentrated nitric acid without change; after long keeping, the nitrate separates from the solution in fine crystals.

Commercial phosphine is always more or less pure chrysaniline nitrate. Usually it contains both the above-mentioned homologues. It is fairly easily soluble in hot water. When this solution is treated

with an equal volume of concentrated nitric acid, the salt is obtained, after cooling, in the form of a conglomeration of slender, yellow, crystalline needles. Mineral acids do not change the colour of the solution of chrysaniline. Concentrated sulphuric acid dissolves the dye with a yellow colour; fuming acid changes it partly into a sulphonic acid. A solution of chrysaniline is decolorised by zinc dust, but the colour is rapidly restored in the air. Chrysaniline is a fine yellow dyestuff, the shade tending slightly towards the red side.

Wool, silk, and tannin-mordanted cotton are directly dyed by chrysaniline in a neutral bath. It has to a great extent been displaced by chrysoidine, auramine, and other yellow basic dyes.

*Preparation.*—Chrysaniline is obtained as a by-product in the manufacture of rosaniline by means of arsenic acid or nitrobenzene. It is isolated, by careful, partial precipitation, from the mother liquors of the magenta, and is finally purified by crystallisation from concentrated nitric acid.

**Leather Yellow.**—Under this name is placed on the market a yellow dyestuff, which is obtained as a by-product from the mother liquors in the manufacture of magenta. Leather yellow is a very impure product which contains chrysaniline and probably also other yellow dyestuffs. It is employed in leather dyeing.

**Grenadine** (*Grenat, Cerise*).—These names denote commercial dyestuffs which are obtained as by-products in the manufacture of rosaniline. They usually still contain a considerable quantity of rosaniline, together with chrysaniline and violet dyestuffs (*mauveine?*). Such products exhibit the characteristics of rosaniline in their nature and method of dyeing. The shades are not very pure and are usually rather yellow. They are employed especially in leather dyeing, and are also used in mixtures.

**Rheonine A and N** (*B.A.S.F.*).—Rheonine is obtained by heating *m*-aminophenylauramine, produced from Michler's ketone and *m*-phenylenediamine hydrochloride. The dyestuff dissolves in water with a brown colour; the solution is fluorescent and dyes tannin-mordanted cotton and leather yellowish brown. The aqueous solution is reddened by hydrochloric acid; sodium hydroxide produces a brown precipitate. The solution in concentrated sulphuric acid is brown and fluorescent.

Other dyestuffs of this class are **Coriphosphine** (*By.*) and **Brilliant Phosphine 5G** (*Leonhardt*).

#### XI. HYDROXYKETONE DYES.

**Gallacetophenone, Alizarin Yellow C** (*B.A.S.F.*) is produced by the action of glacial acetic acid on pyrogallol in the presence of zinc chloride. It forms glistening pearly leaflets (melting point 168°) or a

yellowish paste, which dissolves easily in hot water and in alcohol. Alizarin yellow C dissolves in sodium hydroxide with a brown, in concentrated sulphuric acid with a yellow, colour. It produces a fine very stable yellow with aluminium mordants.

Similar reactions are shown by **Alizarin Yellow A**, which is prepared from benzoic acid and pyrogallol. The commercial product is a yellowish grey paste which dyes cotton mordanted with alumina golden-yellow.

**Galloflavin** (*B.A.S.F.*) is closely related to these dyestuffs in its properties. It is obtained by the oxidation of an alkaline solution of gallic acid with atmospheric oxygen. The commercial product is a paste. The substance is insoluble in water, but dissolves easily in alkali hydroxides. Concentrated sulphuric acid produces a yellow solution.

Galloflavin is fixed by metallic mordants like the anthracene dyes. With alumina, and particularly with zinc oxide, it produces a beautiful yellow. The iron lake is green.

**Resoflavin** (*B.A.S.F.*)<sup>1</sup> probably also belongs to this class. It is a pale yellow, fairly liquid paste, which is sparingly soluble even in hot water. Hydrochloric acid or sulphuric acid is without action; the paste is coloured orange-brown by sodium hydroxide.

Chromed wool is dyed in reddish yellow shades, which are fast to light and milling.

## XII. INDIGO AND THIOINDIGO DYES.

The so-called propiolic acid (*o*-nitrophenylpropiolic acid), soon after its discovery, was employed in printing, but not to a great extent. It has been displaced by two other products, which are more cheaply obtained and are not so inconvenient to fix.

**Indigo Salt** (*Kalle*) is the sodium hydrogen sulphite compound of *o*-nitrophenyl- $\beta$ -lactic acid methyl ketone, and is brought on the market in the form of a white paste. Indigo salt is soluble in water at 38—45°; at higher temperatures the solution becomes turbid owing to the separation of the ketone, which redissolves, however, on cooling. Indigo is produced by treatment with an alkali. The bisulphite compound is no longer a commercial product on account of its slight stability, the ketone itself being placed on the market under the name Indigo Salt T. The soluble bisulphite compound is prepared by the dyer himself.

**Indophor** (*B.A.S.F.*), produced by heating phenylglycine-*o*-carboxylic acid with an alkali hydroxide, is indoxyl acid. It is a greenish grey powder, which decomposes into carbon dioxide and indoxyl in the

<sup>1</sup> *Rev. Gen. Mat. Col.*, 1899, 3, 125.



presence of water, especially on warming. Indigo is precipitated when the alkaline solution is shaken with air.

The quality of this product is determined by print-trials or by the conversion of a weighed amount into indigo.

**Indigo Pure** (*B.A.S.F.*), in paste 20 per cent., in paste S; in powder.

Since 1897 synthetic indigo has been brought on the market in the form of a powder or paste, under the name "Indigo Pure." It is prepared from phenylglycine-*o*-carboxylic acid by Heumann's process. The powder consists of nearly pure indigotin; it contains moisture and a very small quantity of inorganic matter. Synthetic indigo is also manufactured by other firms.

**Indigo MLB**, Paste 20 per cent. (*M. L. Br.*); **Indigo MLB, R**, Paste 20 per cent.; **Indigo MLB**, in powder; **Indigo MLB, G**, in powder; **Indigo MLB Vat L** 20 per cent.; **Indigo TRG** (*Geigy*); **Indigo Pure** 93/94 per cent. (*Soc. Chim. des Usines du Rhône*).—The examination is carried out like that of natural indigo (see below).

Some of the homologues of indigo are now found in commerce as also the halogen derivatives. These are prepared generally by dissolving indigo in an indifferent solvent and treating the solution with chlorine or bromine. The following are the more important dyes of this class.

**Indigo MLB/T** (*M. L. Br.*), **Indigo B.A.S.F./G** (*B.A.S.F.*) is 7:7'-dimethylindigo.<sup>1</sup>

**Indigo MLB/R** (*M. L. Br.*), **Indigo B.A.S.F./R** (*B.A.S.F.*) is 5-bromoindigo.

**Indigo MLB/RR** (*M. L. Br.*), is a mixture of mono- and dibromoindigo (5- and 5:5'-).

**Indigo RBN** and **RB** (*B.A.S.F.*), **Indigo, MLB/2B** (*M. L. Br.*) is dibromoindigo.

**Ciba Blue B** (*Soc. Chem. Ind., Basle*) is 5:7:5'-tribromoindigo.

**Bromindigo FB<sup>2</sup>** (*Bayer*), **Indigo MLB/4B** (*M. L. Br.*), **Ciba Blue 2B** (*Soc. Chem. Ind., Basle*) is 5:7:5':7'-tetrabromoindigo.

**Indigo MLB/6B** (*M. L. Br.*) is pentabromoindigo.

Mixtures of indigo and its halogenated derivatives can be separated by extraction with various solvents.<sup>3</sup>

**Ciba Heliotrope B** (*Soc. Chem. Ind., Basle*) is tetrabromoindirubin.<sup>4</sup>

**Thioindigo Red B** (*Kalle*), **Vat Red B**, the representative of a new class of dyestuffs of the indigo group was discovered by Friedlaender. It is prepared from phenylthioglycol-*o*-carboxylic acid by boiling with

<sup>1</sup> Felsen, *Z. Farb. Ind.*, 1909, 8, 215, 231, 247, 263.

<sup>2</sup> Werner, *Färber-Zeit.*, 1909, 20, 185; Grandmougin, *Ber.*, 1909, 42, 4408.

<sup>3</sup> Binz and Marz, *Z. angew. Chem.*, 1909, 22, 1757.

<sup>4</sup> Engi, *Chem. Zeit.*, 1908, 32, 1178.

alkalis, heating the product with acids and oxidising the thioindoxyl produced. Its formula is  $C_{16}H_8O_2S_2$ . It comes on the market as a 20 per cent. paste, which gives a clear yellow vat which dyes in bright red shades.<sup>1</sup>

**Thioindigo Scarlet R** (*Kalle*) is prepared by condensing 3-oxy-(1-) thionaphthen with isatin. Its formula is  $C_{17}H_9O_2NS$ . It appears on the market as a paste which gives a yellow vat dyeing fibres in yellowish red shades.<sup>2</sup>

**Ciba Bordeaux B** (*Soc. Chem. Ind., Basle*) is 5:5'-dibromothioindigo.

**Ciba Red G** (*Soc. Chem. Ind., Basle*) is dibromothioindigo scarlet.

**Ciba Violet A, B and R** (*Soc. Chem. Ind., Basle*) also belong to the group of halogenated thioindigos.

**Ciba Green G** (*Soc. Chem. Ind., Basle*) is dibromo- $\beta$ -naphthindigo.

Other dyestuffs of this class are **Helinden Red B** and **3B, Helinden Scarlet S, Thioindigo Violet, Ciba Scarlet G** (prepared by condensing acenaphthenquinone and  $\alpha$ -oxythionaphthen), etc.<sup>3</sup>

### XIII. SULPHIDE DYESTUFFS.

Under the name "**Cachou de Laval**," a product is employed in dyeing, which was first obtained by Croissant and Bretonnière by fusing sawdust, bran, etc., with sodium sulphide, and possesses the remarkable property of directly dyeing cotton from an alkaline bath, the colours being subsequently shaded on the fibre by treatment with metallic salts.

In recent years Vidal and others have employed simple derivatives of benzene, naphthalene, diphenylamine, and of anthraquinone for the purpose of preparing new sulphur dyestuffs, some of which have already acquired great importance; the chief ones are described below.

**Cachou de Laval** is soluble in water, has an unpleasant odour, and dyes cotton brown. **Cachou de Laval S** is obtained by treating the preceding dye with alkali sulphites, and is employed especially in printing.

**Sulphine Brown** (*Lepetit, Dollfuss, and Gansser*).

**Sulphaniline Brown** (*Kalle*).

**Vidal Black** (*Fabr. de Prod. chim. St Denis*) is prepared by fusing *p*-aminophenol (or *p*-phenylenediamine) with sodium sulphide.

Vidal black dissolves in water with a green colour. Cotton is dyed

<sup>1</sup> Knecht, *J. Soc. Dyers and Col.*, 1906, 22, 156; cf. also Alt, *Färber-Zeit.*, 1906, 17, 169, 185; Wray, *J. Soc. Dyers and Col.*, 1907, 23, 70.

<sup>2</sup> Wirther, *Färber-Zeit.*, 1907, 18, 161; *J. Soc. Dyers and Col.*, 1907, 23, 191.

<sup>3</sup> Rosenberg, *Z. angew. Chem.*, 1909, 22, 2129.

In the presence of sodium carbonate and sodium chloride, and is fixed in a bath of potassium bichromate and sulphuric acid, whereby blue-grey to black shades are produced, which are very fast.

**Vidal Black S** is obtained from Vidal black and an alkali sulphite.

The same firm also manufacture **Autogen Black**, **Autogen Grey**, and **Sulphur Blue B**.

**Thiocatechin** and **Thiocatechin S** (*Poirrier*) are related in the same way as Vidal black and Vidal black S. Thiocatechin is prepared by fusing para-diamines and acetyl-nitroanilines with sulphur and sodium sulphide. It dyes cotton brown.

**Italian Green** (*Lepetit, Dolfuss, and Gausser*) is prepared by heating *p*-nitrophenol with sulphur, sodium hydroxide, and copper sulphate.

The commercial product is a black mass which dissolves in water with a green colour. Sulphur is deposited and hydrogen sulphide is evolved from the aqueous solution by the addition of hydrochloric acid.

It produces green shades on cotton in a boiling bath containing 10 per cent. of sodium chloride.

**Immedial Yellow D** (*Cassella*) is prepared from *m*-tolylenediamine and sulphur (at 190°), and **Immedial Orange N** from the same materials (at 250°).

**Eclipse Yellow** (*Geigy*) is obtained by adding benzidine or *m*-tolylenediamine to the product which results on fusing sulphur and mono- or di-formyl-*m*-tolylenediamine.

**Thional Brown R** (*Sandoz*) occurs as a black, coarse powder which dissolves in water with a blackish brown colour. The aqueous solution evolves hydrogen sulphide and gives a brown precipitate on treatment with hydrochloric acid. Sodium hydroxide does not produce any change. The brownish red solution in sulphuric acid becomes turbid on dilution with water owing to the separation of a precipitate. On unmordanted cotton in a boiling bath containing 3 to 5 per cent. of sodium carbonate, and 50 per cent. of sodium chloride, it produces dark-brown shades, which are quite fast to washing and very fast to light, and can be graduated at will by topping with basic dyes in a cold bath containing acetic acid and a little alum.

The same firm manufactures Thional Black and Thional Green.

**Thion Black** (*Kalle*) is prepared by treating dinitrophenol with a quantity of sodium tetrasulphide, insufficient for complete reduction.

Other dyestuffs derived from dinitrophenol are **Immedial Black N** (*Cassella*), **Sulphur Black T extra** (*Akt. Ges.*), and **Thiophenol Black T extra** (*Soc. Chem. Ind., Basle*).

**Thion Green** (*Kalle*) is the product of the reaction between alcoholic sodium hydroxide and *p*-hydroxyphenylthiocarbamide.

**Thion Yellow G** and **GG** (*Kalle*) are derived from thio-*m*-tolylene-diamine.

**Melanogen Blue B** (*M. L. Br.*) is the substance which is obtained by heating the intermediate product, containing zinc chloride, of the naphthazarin melt with sulphur and sodium sulphide.

**Cryogen Brown** (*B.A.S.F.*),<sup>1</sup> prepared from 1:3-dinitronaphthalene, is a black powder which dissolves very easily in water with a brownish yellow colour. The solution is unchanged by sodium hydroxide, but gives a blackish brown precipitate and evolves hydrogen sulphide on treatment with hydrochloric acid. The dyestuff is insoluble in concentrated sulphuric acid or alcohol.

It dyes unmordanted cotton dark brown in the cold in a bath containing sodium chloride.

**Cryogen Blue GR** (*B.A.S.F.*) is also prepared from 1:8-dinitronaphthalene, and can be employed in the presence of sodium chloride.

**Fast Black** (*B.A.S.F.*) is a dyestuff of this class.

**Fast Grey D** and **S** (*Clayton*)<sup>2</sup> are black powders, which are insoluble in water, but dissolve in a solution of sodium sulphide. Concentrated sulphuric acid produces a greyish black or bluish black solution. They are insoluble in alcohol.

Cotton is dyed in grey shades in a solution containing sodium sulphide, sodium hydroxide, and sodium chloride. The fastness of the colours is increased by subsequent treatment with copper sulphate and potassium bichromate.

**Sulpho Black** (*Holliday*)<sup>3</sup> dyes cotton in a bath containing sodium chloride and sodium carbonate.

**Immedial Blue** (*Cassella*)<sup>4</sup> resembles immedial black in its application and properties. Cotton is dyed for one hour at 60—90° in a bath containing sodium carbonate (10 per cent.), sodium sulphide (10 per cent.), sodium chloride (100 per cent.), and dyestuff (10 to 20 per cent.), rinsed at once with cold water, and treated with sodium peroxide or hydrogen peroxide, whereby very fast, indigo-blue shades are produced.

The commercial product is a grey powder, which is insoluble in water and in alcohol. It is slightly soluble in sodium carbonate or ammonium hydroxide, and more so in solutions of sodium hydroxide and alkali sulphides. Concentrated sulphuric acid, in which the dyestuff is insoluble, produces an evolution of a little hydrogen sulphide and sulphur dioxide, and a precipitate of sulphur.

The dyestuff is prepared by heating dinitrohydroxydiphenylamine with sulphur and sodium sulphide.

<sup>1</sup> *Rev. Gen. Mat. Col.*, 1899, 3, 241.

<sup>2</sup> *Ibid.*, 1900, 4, 7.

<sup>3</sup> *Ibid.*, 1900, 4, 7.

<sup>4</sup> *Ibid.*, 1900, 4, 282.

**Thiophor Indigo CJ** (*C. Jäger*) is the leuco compound of 4-hydroxy-3-thiol-*p*-dimethylaminophenyl- $\alpha$ -naphthylamine.

**Immedial Black V extra, G extra** (*Cassella*) is prepared from 2':4'-dinitro-4-hydroxydiphenylamine, and consists of a finely divided, non-hygroscopic powder, which is easily soluble in water. The dyestuff is precipitated from the aqueous solution by acids.

**Immedial Indoné R** (*Cassella*), from *p*-aminotolyl-*p*'-hydroxydiphenylamine, **Immedial Cutch**, **Immedial Direct Blue**, etc., belong to this class, and also **Immedial Sky Blue**, a powder with a bronze lustre, which is insoluble in water and dilute acids, but dissolves in alkali hydroxides, concentrated sulphuric acid, and concentrated hydrochloric acid; it is prepared from *p*-dimethyl-*p*-amino-*p*'-hydroxydiphenylamine, and forms a bisulphite compound which crystallises well.

**Immedial Bordeaux G** and **Immedial Maroon B** (*Cassella*) should also be mentioned.

**Auronal Black** (*Ter Meer*) is prepared from dinitro-*p*-aminodiphenylamine.

**Thion Blue B** (*Kalle*) is derived from *p*-nitro-*o*-amino-*p*-hydroxydiphenylamine.

This class also includes:—

**Catigen Brown N** (*Bayer*) and **Cold Blacks B** and **R** (*Akt. Ges.*)<sup>1</sup> The last two are blackish brown powders, which are slightly soluble in cold water, but dissolve more readily in hot water with a brownish black (B) or violet-black colour. By the addition of hydrochloric acid a violet-black precipitate is produced, which is turned brown by an excess of the acid (B); under the same conditions, brand R gives a blackish brown precipitate, becoming lighter. Sodium hydroxide produces a reddish brown (B) or a violet-black precipitate. The blue solution in concentrated sulphuric acid gives a brown precipitate on dilution with water.

These dyestuffs can be employed on cotton in a cold bath containing 2 to 5 g. of sodium sulphate and 5 g. of soap (per litre). For darker shades, 5 to 15 g. of sodium sulphate, and 3 g. of soap are used. They should be dyed as quickly as possible.

They are well adapted for dyeing mercerised cotton.

**Catigen Indigo RL extra** (*Bayer*) is specially recommended for cop-dyeing.

The following also are included in this class:—

**Eclipse Blue**, **Eclipse Green G**, **Eclipse Black**, **Eclipse Red**, **Eclipse Browns G** and **B** (*Geigy*); **Sulphur Brown G**, **2G**, **Sulphur Cutch R**, **G**, **Sulphur Corinth B**, **Sulphur Blue L extra**, **Sulphur Indigo B** (*Akt. Ges.*); the **Pyrogen** dyestuffs of the *Ges. f. Chem. Industrie*, Basle, of which **Pyrogen Direct Blue** was the first direct

<sup>1</sup> *Rev. Gen. Mat. Col.*, 1899, 3, 125.

blue sulphide dyestuff, and **Pyrogen Yellow M** the first yellow sulphur dyestuff; **Pyranil Black G**, **Thiogen Black**, **Rexoll Black** (*Rexoll Ltd.*), **Thiogen Purple**, **Thiogen Dark Red**  $\frac{3}{4}$  and **R**, **Thiogen Rubin O** (the first red sulphur dyestuff) (*M. L. 3r.*), and the **Thionol** dyestuffs of Levinstein, Ltd.

**Anthraquinone Black**, prepared from dinitroanthraquinone (*B.A.S.F.*),<sup>1</sup> is a blue-black powder, which dissolves easily in cold water with a bluish black colour. Sodium hydroxide changes the colour of the solution to blackish blue. Hydrogen sulphide is evolved and a black precipitate is obtained on the addition of hydrochloric acid. The dyestuff is insoluble in concentrated sulphuric acid and in alcohol. It is employed on cotton in a bath containing 20 per cent. of sodium sulphide, and 100 per cent. of sodium chloride. The mixture is poured in at 60°, and slowly raised to the boiling point; after one hour's boiling, the material is washed carefully, suspended for one hour in the air, and finally passed through a bath containing 5 per cent. of potassium bichromate and 5 per cent. of sulphuric acid.

Twenty to twenty-five per cent. of the dyestuff must be employed to produce a black. The shade is not so blue as that produced by Vidal black.

Sulphide dyestuffs on cotton are identified by heating the material with stannous chloride when hydrogen sulphide is liberated. The sample of cotton should be boiled for one or two minutes in a 10 per cent. solution of sodium hydroxide before applying the test. This removes any admixed sulphur or sulphur compounds, but has no effect on the sulphide dyestuffs. The sample is well washed and heated with stannous chloride in a test tube, the evolution of hydrogen sulphide being detected in the usual way with paper moistened with lead acetate solution.<sup>2</sup>

A comparison of the tinctorial values of black sulphide dyestuffs has been made by Buratti.<sup>3</sup>

<sup>1</sup> *Rev. Gen. Mat. Col.*, 1899, 3, 248.

<sup>2</sup> Green and Stephens, *J. Soc. Dyers and Col.*, 1907, 23, 118.

<sup>3</sup> *Rev. Gen. Mat. Col.*, 1908, 12, 105.

GENERAL PROCEDURE FOR THE CHEMICAL  
EXAMINATION OF DYESTUFFS.<sup>1</sup>

When a technical dyestuff of unknown nature is to be examined, the first experiment, excluding the determination of its solubility in water or alcohol, is always a dye-trial (*cf.* p. 934). By this means the shade is ascertained at once, and moreover the whole behaviour of the substance, with regard to the fabric, can be determined. If the latter does not supply any information the dyestuff is next tested on wool in a neutral bath. All basic dyes, with the exception of methyl green, are completely fixed, and the bath is nearly exhausted. In the case of green dyestuffs it is better first to select silk.

If the dyestuff can be used without a mordant, the next experiment is carried out in the presence of dilute sulphuric acid, alum, or zinc chloride. By the addition of these substances both acid and basic dyes can be fixed. The number of the latter is so limited (alkali blue, alkali green, alkali violet) that their detection presents no difficulty. The recognition of dyestuffs which dye cotton in alkaline solution, and of those which can only be fixed by metallic mordants is equally simple.

Mixtures of different dyestuffs can usually be detected as such by scattering the powdered substance lightly over a filter-paper moistened with water or alcohol. The separate constituents each produce differently coloured spots. Frequently the same object is attained by allowing a drop of the solution to fall on to filter-paper. The colour round the margin of the stain thus produced differs from that in the middle, because the various dyestuffs stain the paper at different rates.

The more important reagents for the identification of known dyestuffs are concentrated sulphuric acid and hydrochloric acid, alkali hydroxides, zinc dust, and also a solution of calcium chloride which is specially used in the case of azo dyes.

Most dyestuffs exhibit characteristic colour-changes by treatment with concentrated acids.

Concentrated sulphuric acid is an excellent reagent for the recognition of mixtures, since frequently it produces entirely different colour-changes in many dyestuffs of otherwise the same shade. A small quantity of the powdered dyestuff is scattered over a few drops of sulphuric acid in a porcelain basin. The presence of different constituents is shown by the formation of differently coloured streaks

<sup>1</sup> *Cf.* Rota, *Chem. Zeit.*, 1898, 22, 437; Gulinow, *Z. Farb. Ind.*, 1906, 5, 337.

in the liquid, which are rendered more distinct by tilting the basin to and fro.

Basic dyes, which are always employed in the form of their neutral salts, frequently exhibit a different behaviour towards alkalis. For example, salts of rosaniline yield a precipitate of the base by treatment with dilute alkali hydroxides, whilst this is not the case with safranine.

The behaviour towards zinc dust and other reducing agents is especially characteristic. Almost all dyestuffs are decolorised by these reagents, but in very different ways. For example, all the azo dyes undergo complete fission in such a way that the dyestuff cannot be easily regenerated from the products of the reduction; other dyestuffs are converted into so-called "leuco bases," which usually oxidise only slightly in the air but can be reconverted into the original dyestuff by a suitable oxidising agent. The latter property is shown by all dyes of the rosaniline series. Again, a third class of dyestuffs are likewise decolorised by reducing agents, but the resulting colourless compound, especially in alkaline solution, very rapidly reproduces the original dyestuff in contact with air. Since this behaviour is quite analogous to that of indigo vats, it is denoted in the sequel by the term "vat formation." For example, a highly coloured alcoholic solution of safranine in the presence of an alkali hydroxide is rapidly decolorised by boiling with zinc dust. If the reduction has been effected in a closed flask from which the air has been previously expelled by boiling, the solution remains quite colourless, but acquires its original colour suddenly when the stopper is removed. This experiment which was first shown by A. W. Hofmann with Magdala red, is equally effective with the more readily obtainable safranine. In addition to these two dyes, mauveine, chrysaniline, and induline exhibit the same behaviour, and also methylene blue in a less degree.

The azo dyes are usually affected by reduction in such a way that the two nitrogen atoms of the azo group become amino groups and are distributed between the original components. For example, an azo dye, obtained by coupling a diazo compound with a phenol, yields by reduction the amine from which the diazo compound was prepared, the second nitrogen atom of the diazo compound entering the phenol in the form of an amino group, thus producing an aminophenol in which the amino group is usually in the para-position. Thus, hydroxyazo-benzene yields aniline, and *p*-aminophenol, according to the equation:—



When a sulphonic acid group is present in either of the nuclei, the corresponding sulphonic acid of the above substance is obtained. In many cases the reductive fission of azo compounds furnishes a good



method of ascertaining their constitution; considerable experience is required, however, in separating the products of the reduction, especially when they both contain sulphonie acid groups.

An acid solution of stannous chloride is a better reducing agent than zinc dust. It reduces most of the azo dyes very easily on warming. The tin is removed by treatment with hydrogen sulphide.

Bases can be separated by adding an alkali hydroxide and extracting with ether, whilst sulphonie acids remain in the alkaline solution. A systematic procedure for the further examination and separation of these substances cannot be given. Frequently recourse must be had to elementary analysis; at other times a few simple reactions suffice.

Most of the commercial dyestuffs and their more important reactions are tabulated in the following pages.

A guide to the "Identification of some of the commonest Dyestuffs on the Fibre" has been published by C. Dreher.<sup>1</sup> The methods are arranged according to the applications of the dyestuffs, cotton dyes being treated first, then wool dyes, and so on. The original publication must be consulted for the details of carrying out the reactions.<sup>2</sup>

These tables contain first mordant dyestuffs (for wool, silk, cotton), then direct dyestuffs (for wool, silk, cotton). The test on the fibre is performed by placing a small piece of the dyed tissue or skein in a porcelain dish and treating it with about 1 c.c. of the solution of the reagent.

The statements in the tables refer to the reactions observed immediately or very shortly after the addition of the reagent. A large number of these reactions have been studied by G. Weber, O. Knecht, and W. Dürsteler.<sup>3</sup> The samples examined in recent years by them are denoted by the name, in brackets, of the firms by which they are manufactured, for which the following abbreviations are employed:—

- (A) = Aktiengesellschaft für Anilinfabrikation, Berlin.
- (B) = Badische Anilin-und Soda-Fabrik, Ludwigshafen.
- (BF) = Basler chemische Fabrik., Basle.
- (By) = Farbenfabriken vorm. Friedr. Bayer & Co., Elberfeld.
- (C) = Cassella & Co., Frankfurt a. M.
- (Cl.Co) = The Clayton Aniline Co., Ltd., Manchester.
- (D) = Farbwerke vorm. L. Durand, Huguenin & Co., Basle.

<sup>1</sup> *Z. Farb. Ind.*, 1902, 1, 415.

<sup>2</sup> Cf. also "Tests of Coal tar Dyestuffs," E. T. Graves, *Leipziger Färber.-Zeit.*, 1904, 53, 154, 161, 185, 193, 203; Matthews, *Textile Colorist*, 1904, 354; Green, Yeoman, and Jones, *J. Soc. Dyers and Col.*, 1905, 21, 236; Green, Yeoman, Jones, Stephens, and Haley, *ibid.*, 1907, 23, 252; Capron, *Rev. Gen. Mat. Col.*, 1906, 10, 129, 206; 1907, 11, 129, 236, 324; 1908, 12, 45, 251, 321, 348; Holden, *J. Soc. Dyers and Col.*, 1909, 25, 47; Green and Frank, *ibid.*, 1910, 26, 83,

<sup>3</sup> *Färber.-Zeit.*, 1903, 14, 139, 162; 1904, 15, 119, 134; 1905, 16, 83.

- (G) = Anilin-und Extrakt-fabriken, vorm. Joh. Rud. Geigy A.-G., Basle.
- (H) = Farbwerke Höchst, vorm. Meister, Lucius, und Brüning.
- (J) = Gesellschaft für chem. Industrie, Basle.
- (K) = Kalle & Co., Biebrich a. Rh.
- (L) = Farbwerk Mühlheim vorm. A. Leonhardt & Co.
- (Lev.) = Levinstein Ltd., Manchester.
- (O) = K. Oehler, Anilin-und Anilinfarben-fabrik, Offenbach a. M.
- (R) = Read Holliday & Sons, Ltd., Huddersfield.
- (S) = Chemische Fabrik vorm. Sandoz, Basle.

The tables are given *in extenso*, although they cannot claim any great value in actual practical work. Such a compilation is, however, very useful for many purposes, as frequent experience has shown.

The abbreviations F and S denote fibre and solution respectively.

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
<b>Black, Violet, &amp; Blue Dyes</b>			
Indigo (Vat-blue), on wool	F. Olive-green; paler blue on dilution S. First yellow, then olive and green, finally dark blue	No action	F. No action S. —
Indigo pure, BASF/RBN(B)	F. Darker S. Light green	...	F. Darker S. Colourless
Logwood, with chromed wool	F. Olive-brown S. Yellow	Violet	F. Slowly red-violet S. Reddish violet
Logwood, with iron-mordanted wool	F. Olive-brown S. Yellow	F. Dull purple S. Pale red	F. Crimson S. Crimson
Chrome black, on wool with indigo ground	F. Dirty red-brown S. Dirty green-yellow; green on dilution	Slight change	F. Redder S. Crimson
Alizarin black, with chromed wool	F. Slight change S. Dirty grey	...	F. Slight change S. Dirty rose
Diamond black, with chromed wool	F. Greener S. Blue-green; violet on dilution	...	F. Dark blue-green S. Colourless
Gallein, with chromed wool	F. Dark brown S. Brownish	Red-violet	F. Dark red S. Amber-yellow
Gallocyanine, with chromed wool	F. Blue S. Deep blue; rose on dilution	F. Slight action S. Slightly violet	F. Violet S. Violet
Celestine blue B, with chromed wool	F. Nearly decolorised S. Bright blue	Redder	F. Red-violet S. Red-violet
Alizarin blue S, with chromed wool	F. Greener S. Dark green-blue	No change	F. Redder S. Pale red
Brilliant alizarin blue, with chromed wool	F. Green-yellow; violet to blue on dilution S. Green	...	F. Bright green; violet on dilution S. —
Alizarin indigo blue, with chromed wool	F. Darker S. Dark red-blue	...	F. Rather darker S. Rose
Alizarin cyanin R, with chromed wool	F. Dark red-blue S. Dark blue; violet on dilution	Darker	F. Redder S. Pale blue
Brilliant alizarin cyanin 3G, with chromed wool	F. Darker; reddish on dilution S. Lilac	...	F. Black; colour restored on dilution S. Slightly yellow; lilac on dilution
Chrome blue, with chromed wool	F. Crimson S. Dirty maroon	...	F. Crimson S. Rose
Chrome violet (Bayer), with chromed wool	F. Orange-yellow S. Yellow	...	F. Bright crimson S. Rose
Chrome patent black TG, with chromed wool	F. Dark green, then brown S. Red	No change	F. Dark red S. Slightly rose
Chrome patent black BT, with chromed wool	F. Green, then red S. Green, then red	No change	F. Slightly blue S. Slightly rose

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
...	Yellow, with green border	F. No action S. —	F. No action S. —	On warming F. Paler S. Greenish yellow
...	F. Bright yellow S. Yellow	...	F. Darker * S. Light yellow	No change
...	Orange, with red border	F. Slowly violet S. —	F. Violet S. Violet	First purple, then brown
...	Yellow-orange	F. Slowly violet S. —	F. Violet S. Violet	First purple, then brown
...	Yellow, with red border	F. Redder S. —	F. Redder S. —	Slight change
...	Olive-brown	F. Green-blue S. —	F. Dark green-blue S. —	Dirty olive-yellow
...	Dark red	F. — S. Blue-grey	F. Darker S. Blue-grey	Decolorised
...	Yellow	F. No change S. —	F. Somewhat bluer S. —	Brown-red
...	Red-brown	...	F. Dirty purple S. —	...
...	Yellow	F. Slight action S. —	F. Decolorised S. —	Decolorised
...	Yellow, with violet border	F. Slight action S. —	F. Blue-green S. Colourless	Dull dark violet
...	Yellow	F. Green-blue S. —	F. Green-blue S. Colourless	Decolorised
...	Dirty yellow, with violet border	F. Greener S. —	F. Greener S. Colourless	...
...	Dirty green	...	F. Greener S. —	Redder
...	F. Dark green S. —	F. Darker S. —	F. Bluer S. —	F. Dark blue S. —
...	Green-yellow	...	...	Somewhat greener
...	Yellow, with red border	F. Paler S. —	F. Paler by keeping S. —	...
No change	Brown-red	No change	Dark blue	Decolorised
No change	Brown	No change	Slightly blue	Decolorised

\* With 5 per cent. NaOH.

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Chrome patent black TR, with chromed wool	F. Green, then brown S. Green, then brown	No change	Dark blue
Chrome patent black T, with chromed wool	Dark green	No change	Blue-green
Azo acid black 3 <sup>BL</sup> , with chromed wool	Carmine-red	No change	F. Reddish S. Rose
Cyananthrol BGA (B)	F. Redder S. Colourless	...	F. Pale dull crimson S. Colourless
Cyananthrol RB (B)	F. Purple S. Colourless	...	F. Purple S. Colourless
Chrome blue R, with wool subsequently treated with potassium bichromate	F. Reddish brown S. —	...	F. Reddish brown S. —
Chrome patent black TG, with wool	F. Green, then brown S. Red	Dark brown	F. Dark brown S. Rose
Chrome patent black BT, wool	F. Brown S. Green, then red	F. Slight change S. Reddish brown	F. Blue S. Rose
Chrome patent black TR, wool	F. Green, then brown S. Green, then brown	F. Slight change S. Reddish brown	F. Brown S. Rose
Chrome patent black T, wool	Green, then dark-green	Very slight change	F. Blue-green S. Reddish violet
Palatine chrome black S (B)	F. Violet, then purple S. Violet, then purple	...	No change
Palatine chrome black 6B (B)	F. Light blue S. Colourless	...	F. No change S. Colourless
Palatine chrome blue WB (B)	F. Little change S. Pale reddish blue	...	No change
Palatine chrome blue W2B (B)	F. Deep violet S. Deep violet	...	No change
Palatine chrome blue BB (B)	F. Black S. Colourless	...	F. Reddish black S. Colourless
Anthracene chrome black PPN extra (C)	F. Violet S. Violet	...	F. No change S. Colourless
Chromate black TB, with wool subsequently treated with copper sulphate and potassium bichromate (A)	F. Black S. Red violet; blue-red on dilution	...	F. Dark red-brown; dark violet-brown on dilution S. Slightly yellow; slightly red on dilution
Domingo alizarin black B, with wool subsequently treated with potassium bichromate (L)	F. Violet tinge S. —	...	...
Melanthren B (B)	F. Olive S. Colourless	...	F. Little change S. Colourless
Azo acid black 3 <sup>BL</sup> , wool	Carmine-red	Slightly reddish	Brick red

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
No change	Brown	No change	Red-violet	Decolorised
No change	Brown-red	No change	Slightly blue	Decolorised
No change	Blue-black	Greenish	Blue	Pale green
...	F. Dull orange yellow S. Colourless	...	F. Greener * S. Colourless	F. Paler and redder S. Purple
...	F. Purple, then brown to orange-yellow S. Colourless	...	No change *	Redder
...	F. Brown S. —	...	F. Violet S. —	...
No change	Reddish yellow	Reddish blue	Dark blue	Decolorised
No change	Brown	F. Slight change S. Wine-red	F. Blue S. Blue	Decolorised
No change	Reddish yellow	Blue-violet	Deep blue-violet	Decolorised
No change	Reddish yellow	Slightly blue	Blue	Decolorised
...	F. Maroon S. Reddish grey	...	No change *	Dull reddish blue (on warming)
...	F. Red S. Yellow	...	F. Light blue * S. Red	F. Light blue S. Blue
...	F. Deep crimson S. Colourless	...	No change *	Little change
...	F. Maroon S. Dull reddish grey	...	No change *	No change
...	F. Yellowish brown S. Dull yellow	...	No change *	Slightly reduced
...	F. Redder S. Light red	...	F. Violet * S. Violet	Decolorised
...	F. Dark brown S. Brownish yellow; brownish on dilution	...	F. Dark violet-brown S. Slightly carmine-red	...
...	F. Dark brown, slowly paler S. —	...	...	...
...	F. Dull yellow S. Colourless	...	No change *	No change
Slightly brick-red	Red-brown	Slightly Bordeaux red	Bordeaux red	Decolorised

\* With 5 per cent. NaOH.

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Naphthol black B, wool	F. Dark blue-green S. Green-blue; violet on dilution	Slight change	F. Slight change S. Colourless
Naphthol black 3B, wool	F. Dark blue-green S. Green-blue	Slight change	F. Slight change S. —
Naphthol black 6B, wool	F. Greener S. Greenish; blue-violet on dilution	Slight change	F. Redder S. Colourless
Naphthylamine black D, wool	F. — S. Blue-black; red-violet on dilution	Slight change	F. Slight change S. Pale green
Anthracite black D, wool	F. Greener S. Greenish grey	Slight change	F. Violet S. —
Victoria black 5G, wool	F. — S. Dirty green	...	F. Greener S. Colourless
Victoria black blue, wool	F. — S. Blue-green	...	...
Jet black R, wool	F. Deep blue S. Deep blue	Slight change	F. Little change S. Slightly green
Wool black, wool	F. — S. Deep blue; violet on dilution	...	F. Brown-purple S. Dirty brown
Nyanza black B, wool	Darker with green tinge	Blue	Blue-violet
Chrome fast black B, wool	Blue	Slight change	Slight change
Nerol B, wool	Blue	No change	Slight change
Nerol BB, wool	Blue	No change	Blue
Biebrich patent black, wool (blue-black)	Blue-green	No change	Slightly reddish
Alizarin blue-black B, wool	Blue-violet	No change	Violet
Azo acid blue 3B conc., wool (H)	F. Violet S. Violet	F. Slowly becomes red S. —	F. Violet, then carmine S. Rose
Wool black 6B, Palatine black 4B, wool	Blue-black	No change	Solution reddish
Wool black 4BF, wool	Blue-black	No change	Violet-red
Wool deep black 2B, wool	Blue-black	No change	Violet-red
Wool deep black 3B, wool	Blue-black	No change	Violet-red
Tabora black X, wool	Blue-black	No change	No change
Amido acid black B, wool (A)	F. Rather dark S. —	F. Rather darker S. —	F. Rather darker S. —
Amido acid black 4B, wool (A)	F. Rather darker and more bluish S. —	...	F. Rather darker S. —
Amido acid black 6B, wool (A)	F. Rather darker and more bluish S. —	...	...
Ortho black 3B, wool (A)	F. Red-brown S. Red on dilution	...	F. Carmine S. Carmine

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
...	Orange-red	F. Blue-violet S. Violet	F. Slight change S. —	Crimson-red
...	Red	F. Blue-violet S. Violet	F. Slight change S. —	Dull crimson
...	Red	F. — S. Pale blue	F. Slight change S. —	Dark purple
...	Brown	F. — S. Pale red-violet	F. Bluer S. Blue	Slight change
...	Greenish yellow, with brown border	...	F. Slight change S. Rose	Deep red-violet
...	Dirty red	F. — S. Blue-violet	F. Dark green S. Green	Decolourised
...	Red-yellow, with red border	F. — S. Red-violet	F. Greener S. Dirty violet	...
...	Yellow, with red- brown border	F. Little change S. —	F. Dark green S. —	Paler, finally colour- less
...	Yellow, with red border	...	F. Slowly becomes dark violet S. Violet	Pale olive-brown, slowly becomes colourless
Bluer	Brown-red	Darker	Greyer	Slight change
Slight change	Dirty brown	Slight change	Slight change	Slight change
No change	Brown-red	Slight change	Slight change	Slight change
No change	Brown-red	Slight change	Slight change	Slight change
No change	Brown-red	Blue	Bluish	No change
Slight change	Brown-yellow	Slight change	Bluish	F. Paler S. Brown-yellow
F. Slowly be- comes red S. —	F. Yellowish brown S. Pale brown	F. Grey-violet S. —	F. Red-brown S. —	F. Becomes slowly tinged with violet S. —
No change	Bordeaux red	Blue	Blue	No change
No change	Deep Bordeaux red	Blue	Reddish blue	No change
No change	Red-brown	Blue	Blue	No change
No change	Brown-red	Blue	Blue	No change
No change	Brown-red	Blue	Reddish violet	Colourless
F. Darker S. —	F. Deep red-brown S. —	F. Rather bluer S. —	F. Bluer S. —	...
...	F. Deep red-brown S. —	F. Rather bluer S. Pale blue	F. Bluer S. —	...
...	F. Deep red-brown S. —	F. Bluer S. Pale blue	F. Bluer S. —	...
...	F. Red-brown S. Rose	F. More violet S. Violet	F. Violet S. —	F. Bluer S. —



Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Sulphoncyanine black 4B (By.)	F. No change S. Colourless	...	F. Lighter S. Violet
Sulphoncyanine black BR (By.)	F. No change S. Colourless	...	F. Lighter S. Light brown
Wool grey, wool	F. Dirty light maroon S. Dirty grey	Grey-violet	F. Lighter S. Brownish maroon
Fast violet reddish, wool	F. Dark deeper grey S. Blue	Brighter	F. Bluer S. Light blue
Fast violet bluish, wool	F. Dark green S. Dark green	Brighter	F. Dark blue-green S. —
Victoria violet 4BS, wool	F. Blue-violet S. Violet	Rather redder	F. Red-violet S. Rose
Red violet 4RS and 5RS, wool	F. Dull yellow S. Yellow	Stronger	F. Nearly decolorised S. —
Acid violet 2B, wool	F. Dull yellow S. Yellow	Greenish yellow	F. Greenish yellow S. —
Acid violet 4BN, wool	F. Reddish yellow S. Yellow	Stronger	F. Bright yellow S. Yellow
Formyl violet S4B, wool	F. Reddish yellow S. Yellow	Bluer	F. Reddish yellow S. Light yellow
Formyl violet 6B, wool	F. Light yellow-brown S. Yellow	No change	F. Yellowish green S. Yellowish green
Alizarin cyanol violet R (C)	F. Dark blue S. Dark blue	...	F. No change S. Colourless
Fast acid violet 10B, wool	F. Green, then greenish yellow S. Yellowish	Bright blue-green	F. Bright green, then amber-yellow S. Yellowish
Alkali violet, wool	F. Bright orange S. Yellow	Blue-green	F. Bright orange S. Yellow
Regina violet, wool	F. Brown S. Dirty brown	Bluer	F. Dark grey S. Light brown
Violamine R, wool	F. Red S. Dirty red	...	F. Bluer S. Rose
Violamine B, wool	F. Bright scarlet S. Dull red	...	F. Blue-violet S. —
Indigo extract, wool	F. Olive-grey; blue on dilution S. Grey	No change	F. Duller S. Light blue
Brilliant sulphonazurin R, wool (By.)	F. Blue-red S. Red	Unchanged	F. Blue-red S. —
Sulphoncyanine G, wool	F. Blue-green S. Light blue	No change	F. Green S. —
Sulphoncyanine 3A, wool	F. Blue-green; blue on dilution S. Blue	No change	F. Dark green; colour restored on dilution S. —

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
...	F. Light brown S. Dark brown	...	F. Blue * S. Colourless	F. Grey S. Colourless
...	F. Decolorised S. Dark brown	...	F. Lighter * S. Brown	Green
...	Green-yellow, with green border	F. Dull brown S. —	F. Dull light brown S. —	Violet
...	Orange-red, with blue border	F. Little change S. —	F. Blue S. Faint violet	Dull red
...	Orange-red, with blue-green border	...	F. Red-blue S. —	Dull red
...	Orange-red	F. Brown-red S. —	F. Brown-red S. Decolorised on warming	...
...	Bright yellow	F. Decolorised S. —	F. Decolorised S. —	Little change
...	Yellow, with green- blue border	F. Decolorised S. —	F. Nearly decolor- ised S. —	Bluer
...	Yellow, with greenish border	F. Decolorised ; colour restored in the air S. —	F. Decolorised S. —	Peacock-green
...	Yellow	F. Lighter S. —	F. Almost decolor- ised S. —	Bright green
Green	Green	Blue	Light grey	Red-brown
...	F. Yellow S. Yellow	...	F. Lighter * S. Blue	F. Lighter S. Colourless
...	Green, with green- yellow border	F. — S. Light blue	...	...
...	Yellow	F. Colourless S. —	F. Colourless S. —	Blue-green
...	Yellow, with blue- green border	F. Decolorised S. —	F. Decolorised (dirty brown) S. —	Much bluer
...	Dull scarlet	F. — S. Rose	F. Cherry-red S. —	Bluer
...	Bright scarlet	F. Redder S. Rose	F. Red-violet S. —	...
...	Yellow, with green border	F. Green S. Light yellow	F. Yellow S. Yellow	Slowly decolorised
F. Dark blue-grey S. —	F. Citron yellow S. —	F. Rather darker S. —	F. Rather darker S. —	F. Rather darker S. —
...	Brownish	F. No action S. Light blue	F. No action S. —	Decolorised
...	Orange	F. No action S. Light violet	F. No action S. —	Decolorised

\* With 5 per cent. NaOH.

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric acid.
Alkali blue 4B, wool	F. Bright red S. Brown-red	No change	F. Redder S. Light green
Water blue, wool	F. Dull red S. Red	No change	F. Brighter S. Light blue
Navy blue HH, wool	S. Little change F. Colourless; reddish on dilution	F. Unchanged S. —	F. Dark brown; colour restored on dilution S. Faint reddish
Navy blue BW, wool	F. Black; reddish brown on dilution S. Colourless; red-brown on dilution	F. Little change S. —	F. Red-brown; colour restored on dilution S. Reddish brown
Patent blue (superfine), wool	F. Greener; becomes dark yellow S. —	Bright emerald green	F. Bright yellow-green; becomes amber-yellow S. Light yellow
Hüchst new blue, wool (H)	F. Yellow-brown (sienna) S. Reddish	Unchanged	F. Green; original colour restored on dilution S. Blue on dilution
Cyanine B, wool	F. Green; becomes dirty yellow S. —	Bright green-blue	F. Bright green-blue; becomes yellow S. —
Indocyanine BF wool, dyed in presence of 5 per cent. of ammonium sulphate (A)	F. Dark green S. —	F. Slowly becomes redder S. —	F. Red-brown S. —
Indocyanine 2R wool, dyed in the presence of 5 per cent. of ammonium sulphate (A)	F. Dark green S. —	F. Slowly becomes redder S. —	F. Red-brown S. —
Orthocyanine B, wool (A)	F. Darker S. —	...	F. Red-violet S. —
Orthocyanine 6G, wool (A)	F. Red-violet S. Carmine	...	F. Carmine S. Carmine
Orthocyanine R, wool (A)	F. Darker S. Violet	F. Rather more violet S. —	F. Carmine; some what bluish S. Carmine
Fast acid blue B, wool	F. Light brown; blue on dilution S. Light brown; light blue on dilution	Little change	F. Yellow; blue on dilution S. —
Thiocarmine R, wool	F. Dark green S. Dirty green; blue on dilution	...	F. Blue-green S. Blue-green
Cyanol AB, wool	Colour destroyed	...	Sp. gr. 1.16 F. Green S. Colourless

10 per cent. Hydrochloric acid.	Nitric acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric acid.
...	Green, with dark border	F. Decolorised S. Light blue	F. Purple-brown S. —	...
...	Green	F. Decolorised S. —	F. Light brown-red S. —	Little change
F. Unchanged S. —	F. Brown S. Faint reddish brown	F. Black S. —	F. Black S. —	F. Little change S. —
F. Unchanged S. —	F. Dark red-brown; black on dilution S. Brown	F. Black S. —	F. Black S. —	F. Blue-black S. —
...	Yellow, with green border	F. Little change S. Colourless	F. Greener S. Light blue	At first bright green, then light yellow
Unchanged	F. Dark green-blue; dull green-yellow on dilution S. Green-blue	F. Decolorised S. —	F. Slowly decolorised S. —	Unchanged
...	Yellow, with green border	F. Brighter S. Light blue	F. Olive-green S. —	...
F. Slowly becomes rather reddish S. —	F. Violet-black, then dark-red brown S. —	...	F. Blue-black, then violet-black S. —	...
F. Slowly becomes rather redder S. —	F. Violet-black, then dark-red brown S. —	...	F. Blue-black, then violet-black S. —	...
F. Slowly becomes blue-violet S. —	F. Reddish brown, then brown S. —	F. More violet S. Violet	F. Violet S. —	F. More bluish S. —
...	F. Red-brown S. Brownish rose	...	F. Darker, and rather more violet S. Violet	...
F. Red-violet S. —	F. Brown S. Yellowish	F. — S. Light violet	F. Red-violet, then carmine S. Carmine	F. Rather more violet S. —
...	Yellow-green	F. Little change S. —	F. Light blue-green S. Colourless	Green
...	Green, with lighter border	F. Rather darker S. —	F. Darker S. —	Rather greener
...	Sp. gr. 1.42 F. Decolorised S. —	...	5 per cent. F. Green S. Light green on warming	F. Light yellow on warming S. —

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Induline NN (water-soluble), wool	F. Brighter and redder S. Blue; on dilution violet	Little change	F. Stronger S. Light blue
Nigrosine (water-soluble), wool	F. Dark violet S. Blue	—	F. Darker S. Reddish blue
Naphthazin blue, wool	F. Green-blue S. Blue-green; red-blue on dilution	Little change	F. — S. Blue
Naphthyl blue, wool	F. Green S. Little change	Little change	F. Little change S. —
Naphthyl violet, wool	F. Green S. Little change	Redder	F. Redder S. —
Methyl violet B, wool	F. Orange; colour restored on dilution S. Yellow	F. Blue-green S. Green-blue	F. Orange; colour restored on dilution S. Yellow
Methyl violet 6B, wool	F. Orange; bright blue on dilution S. Yellow; bright blue on dilution	Green-blue	F. Orange S. Yellow
Crystal violet, wool	F. Orange; green to violet on dilution S. Orange; green on dilution	Dark green	F. Orange S. Yellow
Ethyl violet, wool	F. Orange; green to violet on dilution S. Yellow; on dilution yellow	F. Dark olive-green S. Yellow	F. Orange S. Yellow
Brilliant anthrazurol, wool (B)	F. Black, then brown S. —	—	F. Black, then brown S. Yellow
Alizarin astrol B, wool (By.)	F. Darker and greener, then grey-green S. Slightly rose	—	F. Lilac S. Bluish rose
Victoria blue B, wool	F. Red; colour restored on dilution S. Red	F. No change S. Yellowish	F. Red; colour restored on dilution S. Red
Victoria blue 4R, wool	F. Red; colour restored on dilution S. Red	No change	F. Red; colour restored on dilution S. Red
Night blue, wool	F. Red S. Red	F. Green S. Yellow	F. Bright red S. Red
Xylene blue VS, wool (S)	F. Green, then slowly decolorised S. —	F. Schweinfurt-green S. —	F. Yellow; colour restored on dilution S. Yellow on dilution
Xylene blue BS, wool (S)	F. Green, then slowly decolorised S. —	F. Bluish green S. —	F. Yellow; colour restored on dilution S. Yellow on dilution

10 per cent Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
...	Dark violet	F. Little change S. Colourless	F. Red-violet S. Colourless	Little change
...	...	F. Maroon S. —	F. Dirty maroon S. —	...
...	Dark violet	F. Little change S. —	F. Darker S. —	Duller
...	Brown-red	F. Duller S. —	F. Duller S. —	No action
...	Dark red	F. No action S. —	F. Greyer S. —	No action
...	Yellow, with green border	F. Nearly decolor- ised S. —	F. Slowly decolor- ised S. —	Blue gum
...	Yellow	F. Much lighter S. Colourless	F. Much lighter S. Colourless	Blue
...	Yellow, with darker border	F. Lighter S. —	F. Lighter S. —	Dark green
...	Yellow, with orange border	F. Bluer S. —	F. Bluer S. —	Green
F. Red-violet S. —	F. Dark green S. Blue	F. Sky blue S. Blue	F. Darker S. Blue	...
F. Light lilac S. —	F. Pale lilac, then yellow - brown, finally yellow S. —	F. — S. Light blue	...	...
...	Green-yellow, with red border	F. Dirty violet S. Colourless	F. Dark maroon S. Colourless	Darker
...	Green-yellow, with brown border	F. Slight change S. —	F. Reddish violet S. —	...
...	Red, with green border	F. Grey S. —	F. Reddish brown S. —	Greener
F. Golden-yellow S. —	F. Orange S. —	...	...	...
F. Yellow-green S. —	F. Golden-yellow S. —	F. Lighter and more greenish S. —	F. Light green-blue S. —	F. Greener S. —

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Domingo blue R extra, wool (L)	F. At first dark blue, then brick-red S. —	...	F. Dark blue, brick-red; blue-green on dilution S. —
Methylene blue 4B, wool	F. Olive-green S. Green	F. Little change S. Pale blue	F. Lighter S. Blue
Toluidine blue, wool	F. Dark olive-green S. Greenish	F. No action S. Light blue	F. Slight change S. Blue
Nile blue, wool	F. Red S. Brown	F. Greener S. Light yellow	F. Green-yellow S. Green-yellow
Neutral blue, wool	F. Orange S. Yellow	Bright green	F. Bright orange S. Yellow
Basle blue, wool	F. Olive-green S. Yellow	...	F. Redder; blue on dilution S. Red-violet
Indazine, wool	F. Dirty dark green S. —	F. Little change S. Slightly red-blue	F. Darker S. Blue
Metaphenylene blue B, wool	F. Dirty grey S. —	...	F. — S. Blue
Paraphenylene blue, wool	F. Darker S. Blue	...	F. Darker S. Blue
Indamine blue, wool	F. Much darker S. Bright blue	Darker	F. Darker S. Bright blue
Indoine blue, wool	F. Dark olive-green; blue-violet on dilution S. Olive-green	...	F. Blue-green S. Deeper colour
Lanacyl blue BB, wool	Green	Slight change	Violet-red
Wool violet S, wool	Red	Slight change	Red
Delphine blue B, wool	Red-violet	No change	Red
New patent blue, wool	Green-yellow	Slight change	Colourless
Cyanol extra, wool	Green, then lighter; finally yellow	No change	Green, then becomes yellow
Alizarin saphirol B, wool	Yellow-brown	No change	Brown-yellow
Alizarin irisol R, wool	Dark greenish blue	...	Sp. gr. 1.16. Rather darker
Chromazone blue, wool	Slight change	Slight change	Red
Wool blue BB, wool	Green	Slight change	Yellow
Wool blue R, wool	Green	Slight change	Yellow
Wool blue G, extra	F. Reddish brown; light green on dilution S. Reddish; slightly greenish on dilution	F. Unchanged S. —	F. Reddish brown; blue-green on dilution S. Reddish brown; blue-green on dilution

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
F. Blue-green S. —	F. Brick-red, moss- green S. —	F. Light grey-blue S. —	F. Mauve S. —	F. Rather darker S. —
...	Green	F. Little change S. —	F. Dull blue-violet S. —	...
...	Olive-green	...	F. Dull crimson S. —	Decolorised
...	Brown-yellow, with green border	F. Dark violet S. —	F. Deep crimson S. —	...
...	Green, with yellow- orange border	F. Lavender S. —	F. Much lighter S. —	Green
...	Blue-red	F. No change S. Light blue	F. Darker S. —	Brighter
...	Maroon, with green- ish border	...	F. Redder S. —	...
...	Dull green	...	F. Duller S. —	...
...	Green-yellow	F. Violet S. —	F. Purple S. —	Lighter
...	Dull green	...	F. Purple S. —	...
...	Bright green-yellow	...	F. Violet after keep- ing S. Rose	Greener
No change	Brown-yellow	Slight change	Red	Slowly becomes paler
Red	Yellow	Slight change	More violet	Slowly becomes paler
No change	Brown	More violet	More violet	Rather paler
Greener	Green, at once be- coming yellow	Slight change	Slightly decolorised	Slight change
Green	Yellow	Darker blue	Dirty green	Dark green
No change	Green	Slightly decolorised	Slightly decolorised	Slight change
...	Sp. gr. 1.42 Decolorised	...	5 per cent. F. Light blue S. Blue solution on warming	Decolorised on warming
Slight change	Brown	Slight change	More violet	Paler
Slight change	Brown-yellow	Paler	Paler	Darker, with green tinge
Slight change	Brown-yellow	Slight change	Slight change	Darker, with green tinge
F. Green; blue on dilution S. —	F. Olive; light yel- low on dilution S. Olive	F. Rather duller blue S. —	F. Brown-violet S. —	F. Pale grey S. Reddish



Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Indocyanine B, wool	F. Green S. Green	F. Unchanged S. —	F. Brownish red S. Red
Peri wool blue G, wool	F. Brown-red S. Reddish	F. Unchanged S. —	F. Red S. Red
Erioglaucine, wool	Slight change	Slight change	Yellow
Eriocyanine, wool	Slight change	No change	Yellow-green
Lancyl navy blue, wool	F. Dark green S. Dark green	No change	F. More reddish S. Reddish
Acid alizarin dark blue SN (direct dyeing), wool	F. Dark brown; red on dilution S. Reddish violet; red on dilution	F. Unchanged S. —	F. Reddish brown S. Red
Acid alizarin dark blue SN, wool subsequently treated with chromium fluoride	F. Dark brown-violet; light red-brown on dilution S. Light grey-violet; light reddish brown on dilution	F. Unchanged S. —	F. Brownish S. Light red
Janus blue G, cotton, wool, silk	Dirty yellowish green	No change	Dark green
Janus blue R, cotton, wool, silk	Dirty yellowish green	No change	Dark green
Janus dark blue R, wool	Yellow-green	Rather violet	Greenish blue
Janus dark blue B, wool	Yellow-green	Slightly violet	Greenish blue
Nigrosine (alcohol-soluble), wool	F. Dark slate-greenish S. Dark grey	...	F. Dark slate S. —
Diazine black, silk	F. Dirty olive S. Olive; dirty violet on dilution	F. Rather darker S. —	F. Black S. Red-violet; dirty grey-green on dilution
Diazine blue B, silk	F. Olive S. Green	F. Unchanged S. —	F. Dark green; blue on dilution S. Slightly greenish; blue on dilution
Brilliant diazine blue B, silk	F. Olive S. —	F. Unchanged S. —	F. Green S. Slightly greenish
Brilliant diazine blue 2B, silk	F. Olive S. —	F. Unchanged S. —	F. Green S. —
Silk grey O, water-fast silk	Yellow-green	No change	Greenish
Silk grey R, silk	Yellow-green	No change	Greenish
Helvetia blue, silk	Red	No change	Green-blue
Capri blue, silk	Green	Fades to red	Red
Patent blue, silk	Green, then yellow	Green	Yellow

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
F. Pale violet S. —	F. Brown S. Dull red-brown	F. Little change S. —	F. Dark brown S. —	F. Little change S. —
F. Grey, then brown S. —	F. Yellow-brown S. Reddish brown	...	F. Dark grey-blue S. Violet	F. Unchanged S. —
Slight change	Red yellow	Fades to blue	Tinge in the green	Greener
Slight change	Red yellow	Brighter	Slight change	Slight change
F. More reddish S. Colourless	Dark yellow	F. Blue S. Blue	F. Dark red-brown S. Reddish	Decolorised
F. Unchanged S. —	F. Dark brown S. Blue-violet; red- violet on dilu- tion	F. Blue-black S. Slightly reddish	F. Blue-black S. Slightly reddish	F. Rather lighter red- brown S. —
F. Unchanged S. —	F. Brownish S. Brown-violet	F. Bluer S. —	F. Blue-grey S. Light brownish	F. Little change S. —
No change	Blue-green	No change	No change	Cotton: colourless Wool: colourless Silk: blue-grey, rather weakened
No change	Cotton: yellow- green Wool: yellow-green Silk: bluish green	No change	No change	Cotton: colourless Wool: colourless Silk: blue-grey, rather weakened
No change	Dark green	No change	No change	Light red-brown
No change	Dark green	No change	No change	Light red-brown
...	...	F. Brown S. Grey	F. Purple-brown S. —	...
F. Rather darker S. —	F. Blue-black; dark green on dilution S. Red-violet; grey- green on dilution	F. Unchanged S. —	F. Unchanged S. —	F. Rather paler after a long time S. —
F. Unchanged S. —	F. Green S. Yellowish green	F. Unchanged S. —	F. Unchanged S. —	F. Gradually decolor- ised S. —
F. Unchanged S. —	F. Green S. Slightly greenish	F. Unchanged S. —	F. Unchanged S. —	F. Decolorised S. —
F. Unchanged S. —	F. Green S. Green; blue on dilution	F. Unchanged S. —	F. Duller blue S. —	F. Decolorised S. —
No change	Yellow-green	Slight change	Rather redder	Colourless
No change	Yellow-green	Slight change	Rather redder	Colourless
No change	Blue	Colourless	Brown	Colour diminished
Fades to red Green, then light yellow	Moss-green Yellow	Slight change Slightly decolorised	Lighter Slightly decolorised	Slight change Blue-green

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Patent blue A, silk	Green, then yellow	Slight change	Green, then yellow
Patent blue N, silk	Green, then brown-yellow	Green	Green, then yellow
Patent blue V, silk	Green, then brown-yellow	Green	Green, then yellow
Setopaline, silk (G)	F. Yellow-brown S. —	F. Grass-green S. —	F. Yellow and decomposed S. Yellow
Indol-blue R on cotton mordanted with tannin-antimony	Dark green	No change	Blue-green
Janus dark blue R, cotton	Yellow-green	No change	Greenish blue
Janus dark blue B, cotton	Yellow-green	No change	Greenish blue
Nigrisine, cotton	F. Green-olive S. Greenish	Little change	F. Brownish S. —
Meldola's blue, cotton	F. Black; colour restored on dilution S. Blackish; blue on dilution	...	F. Violet-grey S. Reddish
Brilliant cresyl blue 2B, tannin-mordanted cotton (L)	F. Dark olive S. —	F. Grey-blue S. —	F. Red-brown S. Reddish on dilution
Prune pure, cotton	Blue	Red	Blue
Muscarine J, cotton	Green	Slight change	...
Setoglaucine, cotton	Brown-yellow	Solution, greenish yellow	Orange
Setocyanine, cotton	Brown-yellow	Solution, greenish yellow	Orange
New methylene blue, cotton	Moss-green	Slight change	Green
Gallazine, cotton	Greenish blue	Slight change	Slight change
Coreine AB, cotton	Bordeaux red	Fades to red	Red
Phenocyanine, cotton	Blue-green	Slight change	Paler
Diamine black RO, cotton	F. Deep blue S. Blue	No change	F. Redder S. Colourless
Diamine black BO, cotton	F. Deep blue S. Blue	...	F. Redder S. Colourless
Diamine black BO, developed on cotton with phenylenediamine	F. Deep blue S. —	No change	F. No change S. —
Diamine blue black, developed with resorcinol on cotton	F. Darker S. —	No change	F. No change S. —
Diamine jet black OO, cotton	F. Deep blue S. Violet on dilution	No change	F. No change S. Pale violet
Oxydiamine black N, cotton	F. Dull green-blue S. Dull violet on dilution	No change	F. No change S. —

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
Grass-green	Green, at once becoming yellow	Darker	Darker	Green, fading to yellow
Green, then yellow	Green, at once becoming yellow	Fades slightly	Fades slightly	Green, fading to yellow
Green, then yellow	Green, at once becoming yellow	Fades slightly	Fades slightly	Bluish green
F. Light yellow S. —	F. Yellow and decomposed S. —	F. Somewhat bluer S. —	Unchanged	F. Rather greener S. —
No change	Yellow-green	Violet	Fades to brownish yellow	Fades to red
No change	Dark green	F. Slight change S. Reddish	Reddish	Light brown
No change	Dark green	F. Slight change S. Reddish	Reddish	Light brown
...	At first brownish, then colourless	F. Little action S. —	F. Brownish S. Brownish	Decolorised
...	F. Violet S. Violet	F. Dark red-brown S. Slightly brownish	F. Dark red-brown S. Faint brownish	Green at first, then slowly decolorised
F. Brown S. —	F. Green S. Green	F. Dark blue S. Reddish	F. Brown-orange S. —	F. Decolorised S. —
Red	Grey-green	Fades to violet	Fades to violet	Pale yellow-green
Slight change	Violet-red	Fades slightly	Grey	Colourless
Solution, greenish yellow	Brown-black	Lighter	Slight change	Orange
Solution, greenish yellow	Brown-red	Dark green	Brown-yellow	Orange
Slight change	Dark green	Violet	Red	Colourless
No change	Brown-yellow	Slight change	Dirty red-violet	Paler
Fades to red	Yellow-brown	Bluer	Bluer	Paler
Slight change	Brown-yellow	Slight change	Slight change	Brighter
...	Violet	F. Little change S. —	F. Red-violet S. Rose	Decolorised
...	Violet	F. Little change S. —	F. Redder S. Rose	Decolorised
...	...	F. No change S. —	F. No change S. —	Decolorised
...	...	F. No change S. —	F. No change S. —	Decolorised
.	Dark grey to black solution	F. Redder S. Blue-red	F. Redder S. Blue-red	Decolorised
...	Red-brown	F. Redder S. Light brown	F. Nearly decolorised S. Light red	Decolorised

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Diazo brilliant black-B, developed with $\beta$ -naphthol on cotton	F. Dark blue S. Blue	...	F. Dark green S. —
Violet black, cotton	F. Deep blue S. Blue	Little change	F. Bluer S. Colourless
Columbia black R, cotton	F. Deep red-blue S. Purple on dilution	Little change	F. Little change S. —
Columbia black FF extra, cotton	Green-black	No change	Blue-black
Columbia black EA extra, cotton	F. Black S. Blue	F. Rather darker S. —	F. Rather darker S. Slightly reddish
Columbia black WA extra, cotton	F. Black S. Blue; on dilution dirty red	F. Rather darker S. —	F. Black S. Reddish
Benzo black S extra, cotton	F. Dark violet S. Violet	Greener	F. Dark violet S. Colourless
Benzo grey S extra, cotton	F. Dark violet S. Green-blue	Green	F. Bluer S. Colourless
Benzo fast grey, cotton	F. Greenish grey S. Dirty purple on dilution	...	F. Darker S. —
Neutral grey G, cotton	Black-green	Violet	Blue
Chromanil black F, cotton; grey-black	Blue	No change	Solution brownish yellow
Chromanil black BF, cotton; grey-black	Blue-black	No change	Solution yellow
Chromanil black RF, cotton; grey-black	Blue-black	No change	Solution greenish yellow
Dianil black G, cotton	Blue	No change	F. Bluish S. Reddish
Dianil black R, cotton	Blue	No change	F. Bluish S. Reddish
Direct deep black E, cotton	Bluish violet	No change	Fades to reddish
Diazo black R, cotton	Blue	No change	Fibre bluer
Chromate black 4B (direct colour), cotton	F. Black; on dilution red-brown S. Violet; on dilution red	F. Dark brown S. —	F. Dark brown S. Red
Chromate black 4B on cotton, subsequently treated with potassium bichromate	F. Black S. Grey; reddish on dilution	F. Black S. —	F. Black S. Slightly yellowish
Chromate black 6B (direct colour), cotton	F. Blue-black; on dilution brown S. Blue-violet; on dilution red	F. Dark brown S. —	F. Dark brown S. Reddish
Chromate black 6B on cotton, subsequently treated with potassium bichromate	F. Black S. Slightly grey; on dilution reddish	F. Black S. —	F. Black S. Pale yellow; reddish on dilution

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
...	Purple	F. No change S. —	F. No change S. —	Yellow
...	Red-orange	F. Little change S. Violet	F. Little change S. Rose	Decolorised
...	Dark brown	F. Little action S. —	F. — S. Pale red	Nearly decolorised
No change	Red	Slight change	Slight change	Colourless
F. Rather darker S. —	F. Black S. Brown	F. Black S. Blue	F. Black S. —	F. Reddish brown S. —
F. Rather darker S. —	F. Black S. Brown	F. Black S. Blue	F. Black S. Slightly grey-blue	F. Light brown S. —
...	Yellow-red	F. Red-violet S. Rose	F. Red-violet S. Slightly red	Decolorised
...	Yellow-red	F. Redder S. —	F. Red-violet S. Colourless	Decolorised
...	Light brown	F. — S. Purple	F. — S. Light-brown	Decolorised
Violet	Blue	Slight change	Slight change	Colourless
No change	Solution greyish blue tinged with violet	Slight change	Fades very slightly	Yellowish
No change	Solution red-brown	Fades slightly	Fades very slightly	Brownish yellow
No change	Solution red-brown	Fades very slightly	Fades rather red- dish	Yellowish green
No change	F. Grey-black S. Red-brown	No change	Slight change	Colourless
No change	Grey-black	No change	Slight change	Slightly brown-yellow
No change	Brown-red	...	Slight change	Remains unchanged for a long time
No change	Dirty red-brown	Slight change	Becomes rather violet	Colourless
F. Dark brown S. —	F. Brown-yellow S. Brown-yellow	F. Black S. Pale red-violet	F. Black S. Red	F. Unchanged S. —
F. Black S. —	F. Black S. Pale brown-yellow	F. Blue-black S. —	F. Black S. —	F. Black S. —
F. Dark brown S. —	F. Brown S. Yellow-brown	F. Black S. Red-violet	F. Dark brown S. Crimson	F. Unchanged S. —
F. Black S. —	F. Black-brown S. Brown	F. Black S. —	F. Black S. —	F. Black S. —

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Chromate black T (direct colour), cotton	F. Black; brown on dilution S. Red-violet; on dilution red	F. Dark brown S. —	F. Dark brown S. Red
Chromate black T, on cotton subsequently treated with potassium bichromate	F. Black S. Slightly grey; on dilution reddish	F. Black S. —	F. Black S. Yellowish
Pluto black G, cotton	Brown-black	No change	Violet
Polyphenyl black B, cotton	Blue	No change	Blue
Diphenyl blue-black, cotton	Bluer	No change	More violet
Vidal black, cotton	Green-black	No change	Slight change
Vidal black S, cotton	Blue-black	No change	Slight change
Sulphur black 4B extra, cotton (A)	F. Deep blue-black S. —	F. Deep black S. —	F. Deep black S. —
Sulphur black A extra, cotton (A)	...	...	...
Pyrrol black X conc., on cotton subsequently treated with potassium bichromate, alum, and acetic acid (L)	...	...	F. Blue-black S. —
Pyrrol black RO, on cotton subsequently treated with potassium bichromate, alum, and acetic acid (L)	...	...	F. Blue-black S. —
Pyrrol blue-black, on cotton subsequently treated with potassium bichromate, alum, and acetic acid (L)	...	...	F. Deep black S. —
Immedial black V extra, cotton	Blue-grey	Almost no change (bluish)	Slight change (brownish)
Immedial black V extra, on cotton subsequently treated with potassium bichromate and copper sulphate	Blue-grey	Rather bluish	No change
Thiogen black M conc., cotton	...	...	...
Thiophenol black T extra, cotton	F. Black S. Slightly grey	F. Unchanged S. —	F. Unchanged S. —
Thiophenol black 2B extra, cotton	F. Black S. Dull blue	F. Unchanged S. —	F. Unchanged S. —
Thioxin black (Oe.)	...	...	...
Pyrogen black BD, cotton	F. Unchanged S. Slightly grey-blue	F. Unchanged S. —	F. Unchanged S. —
Pyrogen black G, cotton	F. Black S. Blue: dull grey-blue on dilution	F. Black S. —	F. Black S. —

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
F. Dark brown S. —	F. Yellow-brown S. Slightly brown-yellow	F. Black S. Reddish violet	F. Dark brown S. Red	F. Unchanged S. —
F. Black S. —	F. Black S. Yellowish	F. Black S. —	F. Black S. —	F. Unchanged S. —
No change	Brown-red	Bluer	Bluer	Colourless
No change	Brown-red	Bluer	Bluer	Colourless
No change	Grey	More violet	More violet	Colourless
No change	Fades grey	Slight change	Fades to blue-green	Dirty yellow-brown
No change	Violet	Slight change	Fades to blue-green	Dirty yellow-brown
F. Deep black S. —	F. Deep black S. Slightly yellow-green	F. Deep black S. —	F. Deep black S. —	F. Yellow-brown S. —
...	...	...	...	F. Brown-yellow S. —
...	F. Brownish black S. —	...	...	F. Olive
...	F. Brownish black S. —	...	...	F. Brown-yellow S. —
...	F. Brownish black S. —	...	...	F. Dark olive S. —
No change	F. Brownish S. Bordeaux red	No change	No change	Decolorised
No change	F. Brown S. Bordeaux red	No change	Faint blue	Decolorised
...	...	...	...	F. Greenish brown S. —
F. Unchanged S. —	F. Unchanged S. —	F. Unchanged S. —	F. Unchanged S. —	F. Yellowish brown S. —
F. Unchanged S. —	F. Unchanged S. Slightly reddish grey	F. Unchanged S. —	F. Unchanged S. —	F. Yellowish brown S. —
...	...	...	...	F. Dirty green-brown S. —
F. Unchanged S. —	F. Unchanged S. Slightly reddish	F. Unchanged S. —	F. Unchanged S. —	F. Yellow-brown S. —
F. Black S. —	F. Black S. Dull reddish brown	F. Black S. —	F. Black S. —	F. Light yellowish brown S. —



Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Thionol black HN (Lév.)	F. Little change S. Pale reddish blue	...	No change
Immedial brilliant black 6BG conc. (C)	No change	...	No change
Pyrogen grey B, cotton	F. Black S. Slightly grey-blue	F. Black S. —	F. Black-brown S. —
Diphenyl black base I	F. Unchanged S. Pale blue	...	Sp. gr. 1.16 Unchanged
Diamineral black B, cotton	Blue-violet	Bluish	Blue
Diamineral black B, on cotton subsequently treated with potassium bichromate and copper sulphate	Blue-violet	Bluish	Blue
Zambesi black, cotton	Dark green	Brownish	Brown
Zambesi black, developed on cotton with nitrogen	Blue-violet	No change	Bluish
Zambesi black D, cotton; grey-blue	Fibre and solution green with blue tinge	Fibre reddish violet	F. Dirty brown-yellow S. Bluish
Zambesi black F, cotton; grey-blue	Blue-black	Slight change	F. Slight change S. Slightly bluish
Zambesi black BR, cotton; grey-blue	Green, with bluish tinge	No change	Slight change
Zambesi black V (direct colour), cotton	F. Black S. Dull blue; pale blue on dilution	F. Unchanged S. —	F. Blue-black S. Slightly reddish blue
Zambesi black V, developed on cotton with <i>m</i> -phenylenediamine	F. Black S. Olive; neutral tone on dilution	F. Unchanged S. Slightly reddish	F. Black S. Slightly reddish
Zambesi black 2G (direct colour), cotton	F. Black S. Neutral tone; blue on dilution	F. Black S. —	F. Blue-black S. Slightly grey
Zambesi black 2G, developed on cotton with <i>m</i> -phenylenediamine	F. Black S. Greenish black	F. Black S. Slightly reddish	F. Black S. Slightly brown
Calcutta black 3B (R)	F. Little change S. Blue-black	...	F. Little change S. Colourless
Calcutta black 3G (R)	F. Deep blue S. Deep blue	..	No change
Oxydiamine black A, cotton	Blue	No change	No change
Cuba black R (Petersén), cotton	Blue	No change	Rather blue
Indanthren, cotton	F. Dirty brown-green S. Slightly brownish	F. Unchanged S. —	F. Unchanged S. —

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
...	F. Little change S. Pale dull purple	...	No change *	Deep olive
...	No change	...	No change *	Dull bluish green
F. Black S. —	F. Black-brown S. Slightly reddish violet	F. Black S. —	F. Black S. —	F. Slightly yellowish brown S. —
...	Sp. gr. 1.42 Unchanged	...	Unchanged *	Unchanged
Slightly blue	Light red-brown	Slightly pale blue	Slightly brownish	At first lilac, then decolorised
Slightly bluish	Red-brown	Pale blue	Slightly blue	Decolorised
Brownish	Magenta	Faint violet	Slightly blue	Decolorised
No change	Dark red-brown	No change	No change	Decolorised
Reddish violet	Blue-violet	Fades to slightly grey-blue	Fades to grey-blue	Colourless
Slight change	Blue-green; after some time red- brown	Fades to bluish	Slight change	Colourless
Slight change	Violet, with reddish tinge	Fades to blue	Fades to bluish	Slightly bluish green
F. Unchanged S. —	F. Black S. Neutral tone	F. Black S. Strong green- blue	F. Black S. Slightly greenish blue	F. Becomes decolor- ised S. —
F. Black S. Slightly reddish	F. Black S. Brown	F. Black S. Slightly blue	F. Black S. —	F. Becomes decolor- ised S. —
F. Black S. —	F. Black S. Dull dark green; brown on dilu- tion	F. Black S. Blue-green	F. Black S. Slightly blue- green	F. Slightly brown- yellow S. Slightly yellow
F. Black S. Rather reddish	F. Black S. Dirty brown	F. Black S. Slightly greenish blue	F. Black S. —	F. Slightly brown- yellow S. Light yellow
...	F. Little change S. Pale dull purple	...	F. No change * S. Colourless	Chocolate-brown
...	F. Dark reddish brown S. Reddish brown	...	No change *	No change
No change	Dark red	F. Darker S. Slightly blue	F. Darker S. Slightly blue	Decolorised
No change	Red-brown	Slightly violet	Slightly violet	Decolorised
F. Unchanged S. —	F. Yellow S. Slightly yellow- ish	F. Unchanged S. —	F. Pale blue-green S. —	F. Unchanged S. —

\* With 5 per cent. NaOH.

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Indanthren blue RC (B)	F. Green S. Green	...	F. No change S. Colourless
Indanthren violet R (B)	F. Little change S. Colourless	...	F. No change S. Colourless
Cyananthren B double (B)	F. Greenish blue S. Greenish blue	...	No change
Diazo blue, cotton	Blue	No change	Greyish blue
Glycine blue, cotton	Blue	Rather bluer	Violet
Azo black blue, cotton	Bluer	Bluer	More violet
Phenamine blue, cotton	Green	Slight change	Rather paler
Erie blue GG, cotton	Greenish blue	No change	Greenish blue
Titan Como B, cotton (R)	F. Flesh-coloured S. —	...	F. Greyish blue S. —
Trisulphone blue B, cotton	Greenish blue	Slight change	Darker
Trisulphone blue R, cotton	Greenish blue	Slight change	Darker
Trisulphone violet B, cotton	Dark blue	Slight change	More violet
Oxamine blue RRR, cotton	Dark greenish blue	Slight change	Darker
Oxamine violet, cotton	Dark blue	Slight change	Darker
Rosanthren violet 5R (I)	F. Blue S. Colourless	...	F. Bluish purple S. Colourless
Violanthren BS (B)	F. Little change S. Purple	...	No change
Violanthren CD (B)	F. Grey S. Colourless	...	No change
Ciba violet B (I)	F. Bluish green S. Slightly blue	...	F. Decolorised S. Colourless
Ciba violet R (I)	F. Bluish green S. Pale green	...	F. Bluish red S. Colourless
Ciba Bordeaux B (I)	F. Brown S. Brown	...	F. No change S. Colourless
Ciba heliotrope B (I)	F. Dark brown S. Dark brown	...	F. No change S. Colourless
Zambesi indigo blue, cotton	Bluish green	No change	F. Violet S. Slightly violet
Zambesi indigo blue, developed on cotton with $\beta$ -naphthol	Bluish green	No change	No change
Diaminogen, with $\beta$ -naphthol on cotton	Violet-black	No change	Blue
Diaminogen blue BB, cotton	Bluish violet	No change	F. Rather bluer S. Slightly blue
Diaminogen blue BB, developed on cotton with $\beta$ -naphthol	Reddish grey	No change	F. Rather bluer S. Slightly wine-red
Diamineral blue R, cotton	F. Bluish green S. Bluish green	Rather bluer	Rather bluer

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
...	F. Green S. Colourless	...	F. No change * S. Colourless	No change
...	F. No change S. Colourless	...	F. Redder * S. Colourless	F. Red S. Colourless
...	No change	...	No change *	Black
No change	Brownish red	Slight change	Slight change	Rapidly becomes rose
Rather bluer	Green	Rather redder	Rather redder	Violet, slowly decolorised
Slight change	Dirty brownish red	Slight change	Violet-black	Bluish violet
Slight change	Violet-red	Slight change	Paler	Colourless
No change	Brownish yellow	Violet-blue	Violet-blue	Decolorised
...	F. Grey S. —	F. Decolorised S. —	F. Heliotrope S. —	...
No change	Reddish	Violet	Violet	Violet
No change	Reddish	Slight change	Violet	Violet
No change	Reddish brown	Violet	Violet	Pale violet
No change	Red	Violet	Violet	Pale violet
No change	Dirty violet	Redder	Redder	Pale violet
...	F. Purple S. Colourless	...	F. Redder * S. Colourless	Little change
...	F. Reddish grey S. Colourless	...	No change *	Reddish brown
...	F. Paler S. Colourless	...	No change *	Redder
...	F. Redder S. Colourless	...	F. Bluer * S. Colourless	F. Decolorised S. Colourless
...	F. No change S. Colourless	...	F. No change * S. Colourless	F. Dirty green S. Colourless
...	F. No change S. Colourless	...	F. No change * S. Colourless	F. Decolorised S. Colourless
...	F. Darker S. Colourless	...	F. No change * S. Colourless	Decolorised
No change	Carmine-red	F. Slight change S. Violet	Fades to reddish	Decolorised
No change	Light reddish brown	No change	No change	Decolorised
No change	Red	More violet	Bluer	Colourless
No change	Faint brownish red	F. Slight change S. Slightly blue	F. Violet S. Slightly violet	Decolorised
No change	Light brown	F. Darker S. Slightly reddish	F. Rather bluer S. Reddish violet	Decolorised
Rather bluer	Light reddish brown	F. Slightly violet S. Slightly violet	F. Slightly violet S. Slightly violet	Lilac

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Diamineral blue R, subsequently treated with potassium bichromate, cotton	F. Blue S. Blue	No change	Slightly violet
Naphthamine deep blue R, cotton (K)	F. Sky blue S. —	F. Violet-blue S. —	F. Violet-blue S. —
Naphthamine indigo RE, cotton (K)	F. Sky blue S. —	F. Bluish violet S. —	F. Bluish violet S. —
Benzo indigo blue, cotton, (By.)	F. Bluish green S. —	Unchanged	F. Rather paler S. —
Triazol blue R (direct colour), cotton (O)	F. Bluish green S. —	...	...
Benzo black blue G, cotton	F. Green S. Faint blue	No change	F. Greener S. Colourless
Benzo black blue R, cotton	F. Greenish blue S. Blue	Little change	F. Little change S. —
Azo violet, cotton	F. Greenish blue S. Blue	Blue	F. Blue S. Colourless
Azo mauve, cotton	F. Greenish blue S. —	Paler	F. Blue S. —
Congo Corinth G, cotton	F. Deep blue S. Blue	Blue	F. Blue S. Colourless
Congo Corinth B, cotton	F. Deep blue S. Blue	Violet	F. Reddish blue S. Colourless
Sulphur Corinth B, cotton (A)	F. Black S. —	F. Black S. —	F. Black S. Bluish green
Heliotrope 2B, cotton	F. Violet S. Violet	Little change	F. Bluer S. Colourless
Diamine violet N, cotton	F. Greenish blue S. Greenish blue	Rather bluer	F. Bluer S. Colourless
Trona violet B, cotton (By.)	F. Dark flesh-coloured S. —	Unchanged	F. Bluish rose S. —
Triazol violet R (direct colour), cotton (O)	F. Deep blue S. Bluish rose on dilution	...	F. Deep blue S. —
Azo blue, cotton	F. Greenish blue S. Blue	Little change	F. Little change S. —
Benzoazurin G, cotton	F. Greenish blue S. Blue	Redder	F. Little change S. —
Benzoazurin 3G, cotton	F. Greenish blue S. Blue	Little change	F. Darker S. Colourless
Naphthogen blue 4R (direct colour), cotton (A)	F. Black ; on dilution S. —	F. Violet-blue S. —	F. Bluish green; on dilution violet S. Yellowish; rose on dilution

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
No change	Dark reddish brown	No change	Slightly violet	Decolorised
F. Violet-blue S. —	F. Slowly decolorised S. Brownish	No change	F. Reddish blue S. —	F. Pale bluish violet S. Reddish
F. Bluish violet S. —	F. Slowly decolorised S. Reddish	No change	F. Greyish blue S. —	F. Bluish violet S. —
Unchanged	F. Slowly decolorised S. Brownish	F. Rather darker S. Faint blue	F. Dark greyish blue S. —	F. Paler S. —
...	F. Greenish grey S. —	...	F. Rather darker S. —	F. Rather paler S. —
...	Brownish red	F. No change S. —	F. Rather darker S. Colourless	Decolorised
...	Light brown	F. Violet S. Faint rose	F. Reddish violet S. Colourless	Decolorised
...	Red	F. Crimson S. —	F. Crimson S. Colourless	Decolorised
...	...	F. Rather redder S. —	F. Redder S. —	Decolorised
...	Brown	F. Brighter S. Rose	F. Redder S. Colourless	Decolorised
...	Brown	F. Much redder S. Rose	F. Much redder S. Colourless	Decolorised
F. Black S. —	F. Dark brown S. Bluish green	F. Dark violet S. —	F. Blackish violet S. —	F. Pale olive S. —
...	Reddish orange	F. Little change S. —	F. Crimson S. Colourless	Decolorised
...	Brown	F. Redder S. —	F. Redder S. Colourless	Decolorised
Unchanged	F. Rose; decolorised on dilution S. Rose on dilution	F. Lilac S. Lilac	F. Bluish rose S. —	F. Decolorised S. —
...	F. Dirty red S. —	F. Rather more tinged with red S. —	F. Rather darker S. —	F. Blue S. —
...	Orange	F. Reddish violet S. Rose	F. Magenta red S. Rose	Decolorised
...	Light brown	F. Reddish violet S. Rose	F. Crimson S. Slightly rose	Decolorised
...	Orange	F. Violet S. Rose	F. Reddish violet S. Rose	Decolorised
F. Reddish blue S. —	F. Reddish brown; reddish violet on dilution S. —	F. Dark violet-blue S. Lilac	F. Reddish violet S. —	F. Bluish green S. —

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Naphthogen blue 4R, developed on cotton with $\beta$ -naphthol (A)	F. Black; on dilution bluish violet S. —	F. Violet-blue S. —	F. Dark blue; on dilution violet S. —
Brilliant azurin 5G, cotton	F. Bluish green S. Pale green	Little change	F. Little change S. —
Sulphone azurine, cotton	F. Violet S. Violet	Little change	F. Dirty violet S. —
Diamine deep black SS, cotton	Blue-black	Slight change	Bluish violet
Diamine blue 3R, cotton	F. Greenish blue S. Blue	Little change.	F. Darker S. Colourless
Diamine blue or Benzo blue, BX, 2B, 3B, cotton	F. Greenish blue S. Blue	Redder	F. Violet S. Colourless
Diamine blue 6G, cotton	F. Dirty olive-grey S. —	Little change	F. Little change S. —
Chlorazol brilliant blue 10B (R)	F. Pale dull green S. Dull green	...	No change
Chlorazol brilliant blue 12B (R)	F. Dull greenish black S. Pale grey	...	F. Redder S. Colourless
Chlorazol brilliant blue R (R)	F. Darker and greener S. Deep azure blue	...	F. Little change S. Colourless
Chicago blue B, cotton	F. Greenish blue S. Greenish blue; violet on dilution	No change	F. No change S. —
Melantherin JH, cotton	F. Blue-black; on dilution violet S. Blue; reddish violet on dilution	F. Rather darker S. —	F. Little change S. —
Melanogen blue B, cotton	F. Blackish S. Faint grey	F. Blackish S. —	F. Blackish S. Yellowish
Sulphur blue L extra, cotton*	F. Blackish blue S. Blue; reddish on dilution	F. Black S. —	F. Brownish S. —
Immedial sky blue, cotton	F. Dark blue S. Blue	F. Unchanged S. —	F. Paler blue S. Blue
Pyrogen blue R, cotton	F. Black S. —	F. Black S. —	F. Dark reddish brown S. —
Pyrogen direct blue reddish, cotton	F. Bluish black S. Blue; reddish violet on dilution	F. Black S. —	F. Bluish black S. —
Sulphur indigo B, and subsequent treatment with potassium bichromate and copper sulphate and with acetic acid, on cotton (A)	F. Black S. —	F. Violet-black S. —	F. Greyish black; colour restored on dilution S. —

\* See also "Note on the Diagnosis of Sky-blue Sulphur Dyes," A. Lüttringhaus, *Z. Farb. Ind.*, 1905, 4, 899.

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
F. Dark violet S. —	F. Reddish brown ; on dilution red- dish violet S. —	F. Dark violet-blue S. —	F. Violet S. —	F. Dark bluish grey S. —
...	Crimson	F. Reddish violet S. Colourless	F. Reddish violet S. Colourless	Decolorised
...	Yellow	F. No change S. —	F. No change S. —	Decolorised
Slight change	Brownish red	Darker	Violet	Colourless
...	Orange-yellow	F. Reddish violet S. Rose	F. Magenta red S. Rose	Decolorised
...	Light brown	F. Violet S. Colourless	F. Reddish violet S. Colourless	Decolorised
...	Yellow	F. Little change S. —	F. Redder S. Colourless	Pale violet
...	F. Paler and duller S. Colourless	...	F. Paler and red- der * S. Colourless	No change
...	F. Darker and duller S. Pale blue	...	F. Dull reddish blue * S. Colourless	No change
...	F. Dull slate-blue S. Pale dull blue	...	F. Purple * S. Colourless	No change
...	Light red	F. No action S. —	F. Little action S. —	Decolorised
F. Rather darker S. —	F. Dark grey S. Dull grey	F. Rather darker S. Slightly bluish	F. Darker S. Slightly reddish violet	F. Little change S. —
F. Blackish S. —	F. Brown S. Light brownish red	F. Bluish black S. —	F. Bluish black S. —	F. Light brown S. Slightly yellowish brown
F. Unchanged S. —	F. Black S. Faint brownish red	F. Blue-black S. —	F. Black S. —	F. Light yellow S. —
F. Unchanged S. —	F. Reddish violet S. Reddish	F. Blue S. Slightly greenish blue	F. Rather darker blue S. Slightly blue	F. Instantly decolor- ised S. —
F. Black S. —	F. Black S. —	F. Black S. —	F. Black S. —	F. Light yellowish S. —
F. Black S. —	F. Black ; grey- green on dilu- tion S. Reddish brown	F. Black S. —	F. Blue-black S. —	F. Light yellowish S. —
F. Black S. —	F. Black S. Violet on dilu- tion	F. Darker S. —	...	F. Dirty light yellow S. Brownish

\* With 5 per cent. NaOH.



Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Immedial direct blue OD, cotton (c)	F. Blackish blue S. Blue	F. Brownish black S. —	F. Violet-black S. Blue-green
Thionol blue 2B (Lev.)	F. No change S. Colourless	...	F. No change S. Colourless
Immedial new blue G (c)	F. Dark violet-blue S. Colourless	...	F. Bluish violet S. Colourless
Immedial direct blue 4B (c)	F. Violet S. Colourless	...	F. Violet S. Colourless
Immedial indone BN (c)	F. No change S. —	...	F. No change S. —
<b>Yellow and Orange Dyes</b>			
Fustic, on chromed wool	F. Dark yellow, becoming reddish brown S. Yellow	Little change	Brighter
Quercitron, on chromed wool	F. Greenish yellow; becoming brown S. Yellow	Little change	F. Little change S. Yellow
Weld, on tin-mordanted wool	F. Darker S. Yellow	...	F. Paler and brighter S. Yellow
Persian berries, on tin-mordanted wool	F. Brown S. Yellow	Little change	F. Very slight change S. Yellow
Young fustic, on chromed wool	F. Orange; yellow on keeping S. Yellow	...	F. Darker S. Yellow
Turmeric, wool	Reddish brown	...	F. Terra-cotta, becoming brown S. Light red
Galloflavin, on chromed wool	Discoloured	Little change	F. Greener S. Yellow
Alizarin yellow A, on chromed wool	F. Dull dark yellow S. Faint yellow	...	F. Little change S. ...
Milling yellow, on chromed wool	F. Bright reddish orange S. Reddish orange; light yellow on dilution	No change	F. Crimson S. Reddish orange
Anthracene yellow, on chromed wool	F. Dull dark maroon S. Dirty brownish maroon	Much darker (brown)	F. Very dark purple S. —
Flavazol, on chromed wool	F. Bright scarlet S. Orange	Scarlet	F. Crimson S. Yellow
Diamond yellow G, on chromed wool	F. Dark orange-red S. —	Light reddish brown	F. Dark orange-red S. Light yellow
Patent fustic, on chromed wool	F. Brownish red S. Red	Darker	F. Brownish red S. Pale yellow
Alizarin orange, on chromed wool	F. Darker S. Light brown	F. Little change S. Rather darker	F. Lighter S. Yellow
Cloth orange, on chromed wool	F. Dark violet S. Deep violet	Darker	F. Dark violet S. —

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
F. Violet-black S. —	F. Black S. —	...	...	F. Dirty light green S. —
...	F. Dark blue S. Light red	...	F. No change * S. Colourless	F. Brown S. Colourless
...	F. Dull bluish purple S. Colourless	...	No change *	Dull lemon-yellow
...	F. Violet S. Violet	...	F. No change * S. Colourless	Decolorised
...	F. Redder S. —	...	No change *	Decolorised
...	Dark brown	Darker	F. Rather darker S. Pale yellow	Brighter
...	Yellow	F. Brown S. Yellow	F. Rather darker S. Yellow	Little change
...	Light brown	Brown	F. Orange S. Yellow	Redder
...	Yellow	Browner	F. Browner S. Yellow	Brighter
...	Brownish yellow	F. Orange S. Yellow	F. Reddish brown S. Yellow	Yellower
...	Yellow	F. Scarlet S. Orange	F. Scarlet S. Orange	Reddish brown
...	Dull yellow	F. Little change S. Colourless	F. Rather darker S. Yellow	Paler
...	Greenish yellow	F. Darker S. —	F. Darker S. —	...
...	Orange	F. Redder S. —	F. Browner S. Bright yellow	Decolorised
...	Orange-yellow, with dark purple border	F. Rather darker S. —	F. Darker S. —	...
...	Bright scarlet	No change	No change	Scarlet
...	Bright orange-red	F. Rather darker S. —	F. Rather darker S. —	Light reddish brown
...	Dull red	F. Dark brown S. Light brown	F. Dark brown S. Light brown	Terra-cotta
...	Dirty yellow	F. Redder S. —	F. Redder S. —	Little action
...	Dirty red, with dark violet border	F. Rather darker S. Pale rose	F. Darker S. —	...

\* With 5 per cent. NaOH.

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Metachrome yellow D, chromed wool (A)	F. Dark brown; light brown on dilution S. Reddish	F. Rather darker S. —	F. Dark brown; greenish yellow-brown on dilution S. —
Metachrome yellow RD, chromed wool (A)	F. Dark brown; light brown on dilution S. Reddish violet	F. Yellowish brown S. —	F. Dark brown; yellowish green on dilution S. —
Metachrome yellow 2RD, chromed wool (A)	F. Dark brown; light brown on dilution S. Reddish violet	F. Yellowish brown S. —	F. Dark brown; brownish yellow on dilution S. —
Mordant yellow, wool	Red	No change	Reddish brown
Milling yellow R, on wool subsequently treated with potassium bichromate (L)	F. Orange-red S. —	...	F. Cherry-red S. —
Janus yellow R, cotton, wool, silk	Cherry-red	No change	Red
Picric acid, wool	F. Discoloured; colour restored on dilution S. Yellow on dilution	F. Little change S. Light yellow	F. Decolorised S. —
Naphthol yellow, wool	F. Decolorised S. —	Lighter	F. Decolorised S. —
Naphthol yellow S, wool	F. Browner S. Colourless	Lighter	F. Decolorised S. —
Aurantia, wool	F. Decolorised S. —	Lighter	F. Decolorised S. —
Fast yellow G, wool	F. Bright terra-cotta S. Yellow	F. Orange; bright scarlet on keeping S. Rose	F. Scarlet S. Red
Azoflavine, wool	F. Reddish violet S. —	Darker	F. Reddish violet S. Crimson
Metanil yellow, wool	F. Dark purple S. —	Brownish red, becoming purple	F. Bright purple S. Reddish purple
Jaune solide N, wool	F. Dirty green; on dilution violet S. Violet on dilution	F. Maroon S. Violet	F. Reddish violet S. Reddish violet
Methyl orange, wool	F. Crimson S. —	Crimson	F. Crimson S. Rose
Tropaeolin OO, wool	F. Dark bluish violet S. Violet	Dark maroon	F. Dark reddish violet S. Deep reddish violet
Orange II, wool	F. Bright scarlet, becoming crimson S. Scarlet	...	F. Scarlet to crimson S. Rose
Orange G, wool	F. Crimson S. Red	Little action	F. Scarlet S. Rose
Orange GT, wool	F. Bright crimson S. Crimson	...	F. Bright red S. Rose

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
F. Light reddish brown S. —	F. Dark red; on dilution yellow S. —	F. Unchanged S. —	F. Orange-red S. —	F. Greenish brown S. —
F. Reddish brown S. —	F. Dark brownish red; yellow on dilution S. —	F. Unchanged S. —	F. Orange S. —	F. Greenish dark brown S. —
F. Dark reddish brown S. —	F. Dark brownish red; orange on dilution S. Reddish	F. Unchanged S. —	F. Yellow-red S. —	F. Deep dark brownish green S. —
Redder	Brownish red	Slight change	Orange	Redder
F. Orange-red S. —	F. Cherry-red S. —	...	F. Golden yellow S. —	F. Orange S. —
No change	Cherry-red	Fades faintly yellow	Red	Cotton: colourless Wool: yellowish Silk: yellowish
...	Straw yellow	F. Orange S. Yellow	F. Orange S. Yellow	Lighter
...	...	F. Paler S. Yellow	F. Little change S. Yellow	Decolorised
...	Browner	F. Brighter S. Yellow	F. Little change S. Yellow	Decolorised
...	...	F. Orange S. —	F. Orange-red S. —	...
...	Yellow, with bright red border	F. Little action S. Yellow	F. Darker S. Yellow	Decolorised
...	Red, with purple border	F. Little action S. —	F. Greener and S. — [darker	Lighter
...	Red, with purple border	F. Little action S. —	F. Brighter S. —	Brown, becoming purple
...	Yellow, with orange and maroon border	F. Brighter S. —	...	...
...	Yellow, with crimson border	F. No action S. —	F. Little action S. —	...
...	Red, with maroon border	F. Brighter S. —	F. Brighter S. —	Darker
...	Yellow, with scarlet border	F. Darker S. Pale orange	F. Dull scarlet S. —	...
...	Yellow, with red border	F. No action S. —	F. Terra-cotta S. —	Decolorised
...	...	...	F. Darker S. —	...

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Orange R, wool	F. Crimson S. Red	...	F. Scarlet S. Rose
Crocein orange, wool	F. Orange-yellow S. Red	Brighter	F. Red S. Red
Tartrazine, wool	F. Darker S. Bright yellow	No change	F. Rather darker S. Yellow
Flavazine S, wool (H)	F. Rather darker S. —	Unchanged	F. Darker S. Yellow
Milling yellow O, wool	F. Dark crimson; yellow on dilution S. Bluish red	Rather darker	F. Dull crimson S. Crimson
Quinoline yellow, wool	F. Dull red-yellow S. Pale yellow	...	F. Amber yellow S. Faint yellow
Uranin (Fluorescein), wool	F. Greenish yellow S. Greenish yellow	F. Lighter S. Yellow	F. Brighter S. Yellow
Phosphine, wool	F. Dirty greenish yellow S. Light yellow	Orange	F. Brighter and lighter S. Yellow
Chrysoidine R, wool	F. Yellow-brown S. Yellow	Orange	F. Scarlet S. Rose
Thioflavine S, wool	F. Brown; colourless on keeping S. —	Lighter	F. Decolorised S. —
Resoflavin, wool	F. Unchanged S. Dirty yellow-green	Unchanged	Lighter
Pyramine orange 8G, wool	Yellow-brown	Brownish	Brown
Phenoflavine DFL, wool	Brown-yellow	No change	Red
Acridine yellow, wool	Green-yellow	Slight change	Red
Acridine orange, wool	Green-yellow	Redder	Green-yellow
Auramine G, tannin-mordanted wool (By.)	F. Canary-yellow S. —	F. Orange S. —	F. Rather lighter S. Yellow
Benzoflavine, cotton	F. Much lighter S. —	No action	F. Orange S. —
Auramine O, cotton	F. Olive-yellow S. Yellow on dilution	Lighter	F. Lighter S. —
Auramine G, cotton	F. Brown S. Yellow on dilution	Lighter	F. Decolorised S. —
Thioflavine T, cotton	F. Light red S. Colourless	Orange	F. Lighter S. Yellow
New phosphine G, cotton	Browner	No change	Browner
Flavophosphine GO, tannin-mordanted cotton (H)	F. Light yellow S. Yellowish	F. — S. Pale rose	F. Yellow S. —
Rheonine A, cotton	Yellowish green	No change	Dirty brown-red

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
...	Yellow, with red border	...	F. Terra-cotta S. —	...
...	...	F. Rather darker S. —	F. Browner S. —	Decolorised
...	Orange	F. Brighter S. Light yellow	F. Redder S. Bright yellow	Lighter, slowly decolorised
Unchanged	F. Golden yellow S. —	F. Sulphur yellow S. —	F. Rather lighter S. Yellow	F. Golden yellow S. —
...	Red, with deep maroon border	F. Brighter S. —	...	Decolorised
...	...	F. No change S. —	F. Duller S. —	Rather brighter
...	Little change	F. Redder S. Deep yellow, with intense green fluorescence	F. Orange-yellow S. Yellow, with in- tense fluorescence	Little change
...	Little change	F. Little change S. —	F. Yellow S. —	Nearly decolorised
...	Orange-red	F. Yellower S. —	F. Deeper S. —	Orange
...	...	F. Lighter S. —	F. Much lighter; colourless on keep- ing S. —	Brighter
Unchanged	Red-brown	Unchanged	Almost decolorised	Pale yellow
Yellow-brown	Dark reddish brown	Unchanged	Redder	Decolorised
Redder	Red	Redder	Redder	Paler
Slight change	Brown	Slight change	Faint yellow	Redder
Red	Yellow	Greenish yellow	Greenish yellow	Fading yellowish
F. Orange S. —	F. Orange; decol- ourised on dilution S. —	F. — S. Yellow	F. Golden yellow S. —	F. Orange S. —
...	...	F. Lighter S. —	F. Lighter S. —	Decolorised
...	Brownish	F. Lighter S. —	F. Lighter S. —	Decolorised
...	Straw yellow	F. Redder S. Light brown	F. Nearly decolor- ised S. Light red	Decolorised
...	Brown	F. No action S. —	F. No action S. —	Brown
Redder	Brown-red	Slight change	Darker	Colourless
F. — S. Pale rose	F. Yellow S. Yellow	F. Rather more tinged with yellow S. —	F. Rather more tinged with yellow S. —	F. Rather more tinged with yellow S. —
Slight change	Dirty yellow-green	Slight change	Lighter	Paler

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Tannin orange R, cotton	Red	F. Redder S. Light yellow-red	Red, with blue tinge
Tannin orange B, cotton	Red-violet	Fades orange	Deep red
Alizarin yellow A, cotton	Dirty yellow-green	No change	Fainter
Chrysamin G, cotton	F. Crimson S. Red-violet	Paler	F. Dull crimson S. Colourless
Chrysamin R, cotton	F. Red-violet S. —	Lighter	F. Blue-violet S. —
Cresotin yellow G, cotton	F. Red-violet S. Violet	Yellow	F. Red-violet S. Colourless
Diamine yellow N, cotton	F. Red-violet S. Violet	Lighter	F. Red-violet S. —
Carbazole yellow, cotton	F. Dark green-blue S. Blue	Olive-green	F. Dull violet S. Colourless
Brilliant yellow, cotton	F. Red-violet S. Red	Browner	F. Red-violet S. —
Pyramine orange, cotton	Brown-yellow	No change	Redder
Chrysophenin, cotton	F. Red-violet S. Violet	Little change	F. Violet S. Colourless
Hessian yellow, cotton	F. Crimson S. —	Paler	F. Grey S. —
Curcumin S, cotton	F. Red-brown S. —	Lighter	F. Duller S. —
Naphthamine yellow 2G, cotton (K)	F. Red S. Yellow on dilution	Unchanged	F. Dirty green-yellow; original colour on dilution S. —
Naphthamine orange 2R, cotton (K)	F. Blue S. —	F. Red-brown S. —	F. Dark blue-greenish; original colour on dilution S. Yellowish on dilution
Arnica yellow, cotton (G)	F. Dark carmine-red S. Carmine	F. Yellow-brown S. —	F. Deep blue-violet; colour restored on dilution S. —
Thiazole- or Clayton yellow, cotton	F. Brownish S. Colourless	Orange	F. Orange S. Colourless
Stilbene yellow 2C (Cl.Co)	F. Pale reddish brown S. Reddish	...	No change
Stilbene yellow 3G (Cl.Co)	F. Pale reddish brown S. Brown	...	No change
Stilbene yellow 4G (Cl.Co)	F. Pale reddish brown S. Brown	...	F. No change S. Colourless
Stilbene yellow 8G (Cl.Co)	F. Pale orange-brown S. Colourless	...	F. No change S. Colourless

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
F. Redder S. Light yellow-red	More yellowish orange	No change	F. No change S. Slightly yellow-red	Decolorised
Slight change	Red	Browner	Browner	Slowly decolorised
No change	Yellowish	Browner	Browner	Colourless
...	Red-brown	F. Orange S. —	F. Orange S. —	Decolorised
...	...	F. Orange S. —	F. Rose S. —	Decolorised
...	Violet	F. Orange S. Colourless	F. Red S. Rose	Decolorised
...	Violet	F. Orange S. Colourless	F. Red-orange S. Slightly rose	Decolorised
...	Crimson	F. Rather redder S. Colourless	F. Red-orange S. Rose	Decolorised
...	Dark purple	F. Scarlet S. Rose	F. Scarlet S. Rose	Decolorised
No change	Blue	Brighter	Brighter	Reddish, almost colourless
...	Violet	F. No change S. —	F. No change S. —	Decolorised
...	Dull crimson	F. Orange S. —	F. Scarlet S. —	Decolorised
...	...	F. Redder S. —	F. Redder S. —	...
Unchanged	F. Dull greenish yellow; original colour on dilution S. —	F. Dirty yellow; original colour on dilution S. Yellowish	F. Dirty yellow S. —	F. Rather darker greenish yellow S. —
F. Brown; colour restored on dilution S. —	F. Dark blue-grey; colour restored on dilution S. —	F. Rather lighter S. Reddish	F. Red S. —	F. Decolorised S. —
F. Dark brown S. —	F. Dark red-brown S. Brownish on dilution	F. Orange S. Faint yellow	F. Orange S. —	F. Yellow-brown S. —
...	Decolorised	F. Orange S. Colourless	F. Scarlet S. Colourless	Decolorised
...	No change	...	No change*	No change
...	No change	...	No change*	Slightly reduced
...	F. No change S. Colourless	...	F. No change* S. Colourless	Little change
...	F. No change S. Colourless	...	F. No change* S. Colourless	Little change

\* With 5 per cent. NaOH.



Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Primuline, cotton	F. Duller S. Light yellow	Orange	F. Orange S. Yellow
Primuline, developed with resorcinol on cotton	F. Crimson S. Red	Redder	F. Dark red S. Red
Alkali yellow R, cotton	Red	Orange	Brown-red
Oriol yellow, cotton	Red	Slight change	Red
Direct yellow R, cotton	Red	No change	Dirty yellow-brown
Diamine gold yellow, cotton	Violet	No change	Violet
Diamine fast yellow A, cotton	Red	No change	Brown-yellow
Mimosa, cotton	F. Dull dark yellow S. —	Orange	F. Orange S. —
Congo orange R, cotton	F. Deep blue S. Blue	Brown	F. Violet S. —
Benzo orange R, cotton	F. Blue S. Blue	Green-blue	F. Blue S. Colourless
Tolylene orange R, cotton	F. Brown S. Brown	Red	F. Dark red S. —
Mikado orange, cotton	F. Blue S. —	Yellower	F. Pale olive S. —
Dianil yellow R, cotton	Brownish	Orange	Light yellow
Pyrogen yellow M, cotton	F. Rather darker S. Yellow	F. Lighter brown-yellow S. —	F. Brownish yellow S. Pale yellowish
Sulphur yellow R extra, cotton (A)	F. Lighter S. —	...	...
Pyrrol bronze G, cotton (L)	...	...	F. Lighter S. —
Pyrrol bronze GGG, cotton (L)	...	...	F. Lighter S. —
Pyrrol yellow G, cotton (L)	F. Lighter S. —	...	...
Thionol yellow G (Lev.)	F. Duller S. Pale dull yellow	...	F. Orange-yellow S. Colourless
Algol orange R (By.)	F. No change S. Colourless	...	F. No change S. Colourless
Indanthren orange RT (B)	F. Little change S. Yellow	...	F. Yellow S. Yellow
<b>Green Dyes</b>			
Alizarin green, on chromed wool	F. Deep blue S. Blue	Rather bluer	F. Redder S. Rose
Diamond green, on chromed wool	F. Bluer S. Green-blue	Brighter	F. Bluer S. Pale yellow
Azo green, on chromed wool	F. Light brown S. Dirty yellow	...	F. Light brown S. Dirty yellow

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
...	Yellow	F. No action S. —	F. Orange S. —	Yellow
...	Dark red	F. Darker S. —	F. Dark crimson S. —	Dark red
Orange	Yellow-red	Brighter	Red	Almost colourless
Slight change	Red	Orange	Red	Almost colourless
No change	Dirty yellow-brown	Brighter	Redder	Yellowish, almost colourless
No change	Red-violet	Slight change	Slight change	Colourless
No change	Brown-yellow	Redder	Redder	Paler
...	...	F. Orange S. —	F. Orange-red S. —	...
...	Crimson	F. No action S. —	F. No action S. —	Crimson
...	Brown	F. Scarlet S. Colourless	F. Crimson S. Colourless	Brown
...	...	F. No action S. —	F. Redder S. Colourless	...
...	Dirty olive	F. No action S. —	F. Little action S. —	Dirty olive
Orange	Light yellow	Cherry-red	Cherry-red	Decolorised
F. Little change S. —	F. Lighter yellow S. Yellow	F. Little changed S. —	F. Little changed S. —	F. Initially darker brown - yellow ; slowly becomes lighter S. Pale yellow
...	Deeper	...	...	Yellow-orange
...	...	...	...	...
...	...	...	...	...
...	F. Deeper S. —	F. Rather lighter S. —	F. Rather deeper S. —	F. Deeper S. —
...	F. Golden yellow S. Golden yellow	...	No change *	Redder
...	F. No change S. Colourless	...	F. No change * S. Colourless	F. No change S. Colourless
...	F. Yellow S. Yellow	...	F. No change * S. Colourless	F. Light yellow S. Colourless
...	Brown, with purple border	F. Greener S. —	F. Greener S. —	Grey
...	Red, with green border	F. No action S. —	F. No action S. —	Little change
...	Yellow, with orange border	F. Nearly decolorised S. —	F. Much yellower S. —	Much yellower

\* With 5 per cent. NaOH.

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Gambin on iron-mordanted wool	F. Dull olive-green S. Brown	No action	F. Olive S. Bright yellow
Dioxin on iron-mordanted wool	F. Very dark green S. Green-black; yellow on dilution	Darker	F. Dark red-brown S. Red-brown
Gallanil green	Bordeaux red	No change	Violet-red
Indalizarin green, on wool mordanted with chromium fluoride (D)	F. Dull crimson, decolorised on dilution S. Light carmine, darker on dilution	...	F. Red-violet; on dilution bluish green S. Carmine
Janus green GG: cotton, wool, silk	Moss-green	Blue	Green
Janus green B: cotton, wool, silk	Moss-green	No change	Green
Wool green S, wool	Yellow-green	No change	Brown-yellow
Milling green	Yellow	No change	Almost colourless
Naphthol green, wool	Dark blue-green, gradually destroyed	No change	Slightly blue
Chrome green, on wool mordanted with chromium fluoride (By.)	F. Yellow-green S. —	Unchanged	F. Light brown-yellow S. —
Chrome patent green A, wool	Dark green, gradually destroyed	No change	F. Slight change S. Slightly violet
Domingo chrome green, on wool subsequently treated with potassium bichromate (L)	F. Reddish brown S. —	...	F. Reddish brown S. —
Light green (yellowish), wool	F. Orange S. Yellow	Brighter	F. Orange S. Slightly yellow
Light green (bluish), wool	F. Red-brown S. Dirty yellow	...	F. Brown S. Light brown
Guinea green, wool	F. Yellow-brown S. —	...	F. Yellow-green S. —
Guinea fast green B, wool (A)	F. Grass-green, then greenish yellow, finally yellow S. —	F. Slowly becomes rather more tinged with yellow S. —	F. Yellow S. —
Fast green (bluish), wool	F. Dirty yellow S. —	...	F. Amber-yellow S. —
Cyanol green 6G, wool (C)	F. Moss-green, then dirty yellow S. —	...	F. Dirty orange colour restored on dilution S. Pale orange

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
...	Deep red, with yellow-brown border	F. No action S. —	F. No action S. —	• Little change
...	...	F. Dark brown S. Brown	F. Very dark reddish brown S. Red	...
No change	Brown-yellow	Slight change	Slight change	Brighter
...	F. Light yellow-brown S. —	F. Darker S. —	F. Dark blue-green S. —	F. Lighter S. —
Blue	Cotton: bluish green Wool: green, then light blue Silk: bluish green	No change	Rather darker	Cotton: colourless Wool: blue Silk: pale reddish
No change	Cotton: bluish green Wool: bluish green Silk: yellowish green	Blue-green	Blue	Cotton: yellowish Wool: yellowish green Silk: pale rose
No change	Brown-yellow	Bluer	Bluer	Slight change
No change	Yellow	Slight change	Slight change	Greener
No change	Dark red-brown	Slightly bluish	Pale blue, slowly destroyed	Decolorised
F. Light yellow-green S. —	F. Yellow - brown ; sulphur - yellow on dilution S. —	F. Decolorised S. —	F. Decolorised S. —	Unchanged
No change	Light red-brown	Slightly blue	Blue, slowly destroyed	Decolorised
...	F. Carmine S. —	...	F. Brown S. —	...
...	Yellow, with bright orange border	F. Decolorised S. —	F. Decolorised S. —	Brighter
...	Red-yellow	F. Decolorised S. —	F. Decolorised S. —	...
...	Red-yellow	F. Decolorised S. —	F. Decolorised S. —	...
F. Slowly becomes rather more tinged with yellow S. —	F. Yellow S. —	F. Lighter S. —	F. Lighter S. —	F. Rather lighter S. —
...	Green-yellow	...	F. Greener S. —	Lighter and greener
F. Fawn-brown S. —	F. Yellow-red S. Yellowish	F. Sky-blue S. —	F. Sky-blue S. —	F. Lighter S. —

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Malachite green, wool	F. Yellow ; green on dilution S. Yellow	Darker	F. Bright orange ; green on dilution S. Yellow
Brilliant green, wool	F. Red ; green on dilution S. Red	Lighter	F. Bright yellow ; green on dilution S. Yellow
Azine green, wool	F. Dirty brown S. —	...	F. Violet S. —
Naphthalene green, wool	Dark yellow, slowly destroyed	Gradually becomes yellow	Reddish yellow
Alizarin cyanin green E, wool	Greenish blue-green	No change	Grey
Alizarin dark green W, with potassium bichromate and tartar, wool	F. Slight change S. Reddish	No action	F. Slight change S. Slightly reddish
Italian green, cotton	Darker	No change	Darker
Pyrogen green B, cotton	F. Black S. —	F. Black S. —	F. Black S. —
Pyrogen olive N, cotton	F. Rather darker S. Faint olive	F. Little changed S. —	F. Rather lighter S. —
Sulphur green G extra, cotton (A)	F. Black S. —	F. Dark green S. —	F. Dark grey-blue S. —
Thionol green 2B (Lev.)	F. Blue S. Blue	...	F. Reddish blue S. Colourless
Thionol green 3B (Lev.)	F. Blue S. Blue	...	F. Reddish blue S. Colourless
Thionol green 2G (Lev.)	F. Deep blue S. Deep blue	...	F. Dull blue S. Colourless
Thionol green 3G (Lev.)	F. Deep violet-blue S. Pale blue	...	F. Reddish blue S. Colourless
Thionol brilliant green GX (Lev.)	F. Reddish blue S. Reddish blue	...	F. Bluer S. Colourless
Immedial green G extra (C)	F. No change S. Colourless	...	F. Darker S. Pale green
Immedial olive GG (C)	F. Darker S. Pale brown	...	F. Darker and yellower S. Colourless
Benzo olive, cotton	Blue-black	No change	Blue
Diamine green B, cotton	Blue-black	No change	Blue-black
Eboli green B, cotton (L)	F. Blue-violet S. Blue-violet	F. Rather darker S. —	F. Deep blue-violet ; blackish grey on dilution S. —
Algol green B (By.)	F. Bright green S. Bright green	...	F. Bright blue S. Colourless
Algol dark green B (By.)	F. No change S. Colourless	...	F. Olive S. Olive

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
...	Red	F. Decolorised S. —	F. Decolorised S. —	...
...	Yellow-red	F. Decolorised S. —	F. Decolorised S. —	Yellower
...	Brown	...	F. Darker S. —	Brighter
Gradually becomes yellow	Light yellow	Gradually decolorised	Decolorised	Orange
No change	Brownish yellow	No change	Slight change	F. Slowly lighter S. Pale yellow
No action	Brown	Slightly blue	Blue	Yellow-brown
No change	Fades to brown-red; fibre almost black	...	Yellowish green	Brown-yellow
F. Black S. —	F. Black S. —	F. Dark green S. —	F. Dark green S. —	F. Yellowish brown S. —
F. Little changed S. —	F. Lighter olive S. Yellowish	F. Greener S. —	F. Greener S. —	F. Light yellowish brown
F. Rather darker S. —	F. Dark carmine S. —	...	...	F. Light green, then dirty yellow S. —
...	F. Purple S. Purple	...	F. Blue* S. Colourless	F. Pale olive S. Colourless
...	F. Purple S. Purple	...	F. Reddish blue S. Colourless	F. Pale olive S. Colourless
...	F. Purple S. Purple	...	F. Dull blue* S. Colourless	F. Pale olive S. Colourless
...	F. Bluish purple S. Pale purple	...	No change*	Dull yellowish green
...	F. Purple S. Colourless	...	No change*	Olive-yellow
...	F. Dark magenta S. Light brown	...	F. Dark green* S. Pale violet	F. Pale yellow S. Colourless
...	F. Yellowish brown S. Yellow	...	F. Greener and darker* S. Colourless	Orange-brown
No change	Red-violet	Darker	Brown-black	Colourless
No change	Red-violet	Darker	Green-black	Colourless
F. Deep dark green S. —	F. Dark brown-red; decolorised on dilution S. Red	F. Darker S. Green	F. Dark green S. Green	F. Decolorised S. —
...	F. Decolorised S. Pale bluish green	...	No change*	No change
...	F. Yellower S. Colourless	...	F. No change* S. Colourless	F. Maroon S. Colourless

\* With 5 per cent. NaOH.

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Olivanthren (B)	F. Darker and redder S. Colourless	...	No change
Viridanthren B (B)	F. Reddish blue S. Colourless	...	F. Dull bluish purple S. Colourless
<b>Red Dyes</b>			
(Brazil wood) logwood, on wool mordanted with alum	F. Reddish brown S. Brown	Crimson on keeping	F. Red S. Rose
(Brazil wood) logwood, on chromed wool	F. Greenish brown S. Yellow	Little change	F. Dark crimson S. —
Sandere wood, on chromed wool	F. Brown S. Brown	No change	F. Browner S. —
Barwood, on chromed wool	F. Terra-cotta S. —	No change	F. Redder S. —
Camwood, on chromed wool	F. Dark crimson S. Red	No change	F. Dark crimson S. Colourless
Madder, on wool mordanted with alum	F. Brownish red S. Red	No change	F. Little change S. —
Madder, on chromed wool	F. Little or no change S. Red	Orange	F. Lighter S. Red
Cochineal, on wool mordanted with alum	F. Scarlet S. —	Yellower	F. Scarlet S. —
Cochineal, on wool mordanted with tin	F. Dark purple S. Crimson	Darker	F. Lighter S. Red
Archil	F. Purple to brown; almost colourless on dilution S. Purple; red on dilution	Brighter	F. Lighter S. Red
Alizarin, with alum mordant, on cotton (Turkey red)	F. Little change S. Yellow-red; yellow on dilution	No action	F. Orange to light yellow S. Light yellow
Alizarin V, on chromed wool	F. Dark crimson S. Dirty crimson	Yellower	F. Dark red-brown S. Faint yellow
Alizarin G, on chromed wool	F. Dark crimson S. Dull crimson	Yellower	F. Dark brown S. Faint yellow
Alizarin S, on chromed wool	F. Brown S. Brownish red	Yellower	F. Light brown S. —
Purpurin, on chromed wool	F. Bright crimson S. Crimson	Rather bluer	F. Maroon S. Red
Alizarin Bordeaux B, on chromed wool	F. Deep red-violet S. Deep violet	...	F. Maroon S. Dirty brown
Alizarin maroon, on chromed wool	F. Dark cherry-red S. Deep red	Darker	F. Darker S. Dirty brown
Alizarin S, on cotton, mordanted with alum	F. Magenta-red; on dilution red-yellow S. Magenta-red; on dilution red-yellow	...	F. Dark brown-red S. —

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
...	F. Dull deep olive S. Colourless	..	No change *	Little paler
...	F. Greenish grey S. Pale green	...	No change *	Dull purple
...	Yellow, with red border	F. Maroon S. Violet	F. Dark crimson S. Crimson	F. Scarlet on boiling S. Red
...	Yellow, with red border	F. Violet S. Violet	F. Maroon S. Violet	F. Bright crimson on boiling S. Crimson
...	Greenish brown	F. Dark brown S. Colourless	F. Dark brown S. Brown	F. Brighter S. Rose
..	Greenish yellow	F. Brown S. Colourless	F. Brown S. Brown	Brighter
...	Brown	F. Dark purple S. Colourless	F. Dark purple S. Red	F. Brighter S. Rose
...	Slowly turns orange	F. Rather bluer S. —	F. Bluer S. —	Brighter
...	Yellow, with red border	F. Crimson S. —	F. Purple S. —	Terra-cotta
...	Yellow	F. Red-violet S. —	F. Red-violet S. —	Orange-red
...	Yellow	F. Crimson S. Rose	F. Crimson S. Deep crimson	F. Darker S. Orange-red
...	Yellow, with red border	F. Violet S. Violet	F. Violet S. Violet	Decolorised
...	Orange	F. No action S. —	F. Violet S. Violet	Little change; de- colorised on heat- ing
...	Dull red	F. Blue-violet S. —	F. Blue-violet S. —	F. Light brown on heating S. Yellow
...	Orange-yellow	F. Darker S. Colourless	F. Darker S. —	Brown
...	Bright yellow	F. Purple S. Colourless	F. Purple S. Violet	Terra-cotta
...	Yellow, with orange border	F. Darker S. —	F. Dark purple S. Rose	Brighter
...	Dull red	F. Blue-violet S. —	F. Blue-violet S. Blue	...
...	Brownish yellow, with brown border	F. Darker S. —	F. Darker S. —	...
...	Orange-red	F. Purple S. —	F. Purple S. Pale red	Decolorised on heating

\* With 5 per cent. NaOH.



Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Janus red B: cotton, wool, silk	Blue-green	No change	Blue
Janus Bordeaux B: cotton, wool, silk	Blue-green	No change	Blue
Cloth red G (Oehler), wool	F. Violet S. Deep blue	No change	F. Dark red-violet S. Pale blue
Cloth red B (Bayer), wool	F. Dark navy-blue S. Blue-black	No change	F. Dark violet S. —
Cloth red 3G (Bayer), wool	F. Dark navy-blue S. Blue-black	No change	F. Dark violet S. —
Clayton cloth red, wool	F. Purple; red on dilution S. Violet; red on dilution	Brighter	F. Dull crimson S. —
Ponceau 2G, wool	F. Much darker S. Scarlet	No change	F. — S. Rose
Ponceau R (xylidine scarlet), wool	F. Darker S. Rose	Brighter	F. Duller S. Rose
Ponceau 2R (xylidine scarlet), wool	F. Crimson S. Crimson	Little change	F. Rather darker S. Rose
Ponceau 3R (xylidine scarlet), wool	F. Bluier S. Bluish scarlet	No change	F. Little change S. Rose
Palatine scarlet A, wool	F. Crimson S. Magenta-red	...	F. Darker S. Rose
Biebrich scarlet, wool	F. Dark green S. Blue-green	No change	F. Red-brown S. —
Crocein scarlet 3B, wool and cotton	F. Dark blue S. Deep blue	...	F. Dark blue S. Light blue
Crocein scarlet 7B, wool	F. Dark blue S. Blue	Rather darker	F. Dark blue S. Light blue
Crocein 3BX, wool	F. Purple S. Purple	...	F. Crimson S. Rose
Brilliant crocein M, wool	F. Violet S. Violet	...	F. Dark red-blue S. Light blue
Brilliant ponceau 4R, wool	F. Purple S. Purple	...	F. Little change S. —
Crystal ponceau 6R, wool	F. Deep violet S. Deep violet	No change	F. Crimson S. —
Azoecsin, wool	F. Purple S. Purple	...	F. Crimson S. Rose
Double brilliant scarlet 3R, wool	F. Dark violet S. Red violet	Brighter	F. Red violet S. —
Ponceau S extra, wool	F. Bluier S. Blue	No change	F. Brown S. Slightly blue

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
No change	Cotton: dirty brown-red Wool: { Blue-green, then brown- Silk: {   yellow	No change	Bluish violet	Cotton: reddish Wool: red-violet Silk: red-violet
No change	Cotton: dirty blue, then red-brown Wool: { Dirty blue, then brown- Silk: {   yellow	Red-violet	Reddish violet	Red-violet
...	Dirty red, with dark violet border	F. Rather darker S. —	F. Much darker S. —	...
...	Yellow, with dark purple border	F. Crimson S. Rose	F. Crimson S. —	Rather bluer
...	Yellow, with dark purple border	F. Brighter S. —	F. Darker S. —	...
...	...	F. Brighter and rather darker S. Rose	F. Crimson S. —	Rather darker
...	...	F. — S. Rose	F. Orange-red S. —	...
...	Yellow, with orange border	F. Brighter S. —	F. Yellower S. —	Very slowly de- colorised
...	Dirty yellow, with light crimson border	F. Brighter S. Rose	F. Orange-red S. —	Very slowly de- colorised
...	Yellow	F. Little change S. Colourless	F. Red-orange S. Light red	Very slowly de- colorised
...	Yellow, with orange border	F. Lighter S. —	F. Red-brown S. —	...
...	Grey-blue	F. No change S. —	F. Bluer S. Violet	Decolorised on warming
...	Yellow, with blue border	F. — S. Rose	F. Purple S. —	Decolorised
...	Dark blue	F. Brighter S. Rose	F. Brownish purple S. —	Brown
...	Yellow	F. Browner S. —	F. Red-brown S. —	Decolorised on boiling
...	Green-blue, with dark blue border	F. Bluer S. —	F. Purple S. —	Decolorised
...	Yellow, with brown border	F. Rather darker S. Rose	F. Brown S. Light brown	...
...	Yellow, with crim- son border	F. — S. Rose	F. Brown S. —	...
...	Yellow	F. Orange S. Orange	F. Orange S. —	Decolorised
...	Yellow, with red- violet border	F. Rose S. —	F. Rather darker S. —	Decolorised
...	Yellow, with brown border	F. Bluer S. Bluish rose	F. Violet S. —	Crimson

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Ponceau SS extra, wool	F. Red-orange S. Rose	...	F. Yellower S. Rose
Ponceau 6R, wool	F. Violet S. Blue-violet	No change	F. Crimson S. Rose
Azocardinal G, wool	F. Orange-yellow S. Bluish rose on dilution	...	F. Bluish rose S. —
Fast red A, wool	F. Deep blue-violet S. Violet	No change	F. Dull purple S. —
Fast red B, wool	F. Violet S. Blue-red	No change	F. Dull crimson S. Rose
Fast red C, wool	F. Reddish violet S. Violet	No change	F. Darker S. Rose
Fast red D, wool	F. Violet S. Violet	No change	F. Darker S. Rose
Fast red E, wool	F. Dark purple S. Purple	Brighter	F. Red-maroon S. Rose
Fast red BT, wool	F. Violet S. Violet	...	F. Darker S. —
Azo acid rubin, wool	F. Dark blue-violet; red on dilution S. Blue-violet; red on dilution	F. Unchanged S. ...	F. Dark brown-red S. Red
Palatine red, wool	F. Deep blue S. Blue	Little change	F. Blue S. —
Roxamin, wool	F. Blue-violet S. Violet	Little change	F. Blue S. —
Ponceau 10RB, wool	F. Blue S. Deep green-blue; crim- son on dilution	Little change	F. Dark blue-violet S. —
Bordeaux G, wool	F. Bright deep blue; red on dilution S. Dark blue; red on dilu- tion	No change	F. Blue-violet S. Light blue
Bordeaux extra or Congo violet, wool	F. Violet S. Violet	...	F. Dark violet S. —
Brilliant Bordeaux S, wool	Blue	No change	Violet-red
Domingo alizarin Bordeaux, on wool subsequently treated with potassium bichromate (L)	F. Dark red-violet S. —	...	F. Darker S. —
Kiton red S, wool	F. Little changed S. Slightly reddish	F. Unchanged S. Slightly reddish	F. Little change S. Slightly reddish
Archil substitute G, wool	F. Dark purple S. Light purple	No change	F. Crimson S. Pale rose
Archil substitute V, wool	F. Crimson S. Crimson	Darker	F. Crimson S. Light crimson
Archil substitute 3VN, wool	F. Crimson S. Crimson	Darker	F. Crimson S. Light crimson

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
...	Yellow, with orange border	F. Much yellower S. —	F. Orange S. —	...
...	Yellow	F. — S. Rose	F. Brown S. —	...
...	Yellow	F. — S. Pale red	F. Deep red-brown S. —	Decolorised
...	Yellow, with dark red border	F. Darker S. —	F. Maroon S. —	Lighter
...	...	...	F. Brownish red S. —	Lighter
...	Yellow	F. Brighter S. Rose	...	Lighter
...	...	F. Darker S. Brownish	F. Dirty brown S. —	Lighter
...	Yellow, with dull scarlet border	F. Darker S. Red	F. Dark red-brown S. —	Brighter
...	Yellow, with purple border	F. Darker S. —	F. Brick-red S. —	Lighter
F. Unchanged S. —	F. Yellowish red S. Yellowish red	F. Red S. Red	F. Brown-red S. Carmine-red	F. Slightly brighter red S. —
...	...	F. Redder S. —	F. Brown S. Light brown	Nearly decolorised
...	Yellow, with blue border	F. Purple S. —	F. Brownish purple S. —	...
...	Orange	F. — S. Rose	F. Violet-brown S. —	Decolorised
...	...	F. Rather darker S. —	F. Dark-purple S. —	...
...	Yellow, with blue border	F. Crimson S. Rose	F. Dark maroon S. Reddish brown	Bluer
Fading to faint red	Orange-yellow	Fading	Fading red-brown	Slowly decolorised
...	F. Dark red, slowly paler S. —	F. Rather lighter S. —	F. Light red S. —	F. Darker S. —
F. Unchanged S. Slightly red-dish	F. Orange S. Reddish yellow	F. Unchanged S. —	F. Yellowish brown S. Faint yellowish brown	F. Unchanged S. —
...	Yellow, with pale crimson border	F. Brighter S. Light red	F. Rather darker S. —	...
...	Yellow	F. Light maroon S. —	F. Maroon S. —	Lighter
...	Yellow	F. Maroon S. —	F. Dark maroon S. —	Lighter

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Archillin 2B, wool	F. Dark blue S. Blue	No change	F. Violet S. —
Archil Red A } wool Union fast claret }	F. Dark blue S. Blue	...	F. Violet S. —
Orthocerise B, wool (A)	F. Rather deeper, then fiery red S. Rose on dilution	...	F. Cinnabar-red S. —
Azofuchsin G, wool	F. Bluish violet S. Violet-black	No change	F. Brighter S. Rose
Azofuchsin B, wool	F. Dull crimson S. Dirty red	No change	F. Little change S. Rose
Azofuchsin GN extra, cotton	Violet-red	Fades slightly	Rather more violet
Milling-red R, wool	F. Deep red-blue S. Red-blue	Rather darker	F. Brownish maroon S. —
Benzo fast red, wool	F. Crimson; on dilution red-orange S. Crimson; on dilution red-orange	...	F. Crimson S. Crimson
Milling scarlet B (Cl.Co)	F. Crimson S. Crimson	...	F. Bluer S. Colourless
Acid magenta, wool	F. Brown-yellow S. Colourless; on dilution rose	Little change	F. Much paler S. Rose
Azo carmin and rosinduline, wool	F. Dark green S. Light green	No change	F. Darker S. Red
Eosin (yellowish), wool	F. Bright orange, becoming brownish yellow S. Canary-yellow	Bright reddish yellow	F. Bright reddish yellow S. —
Erythrin (methyleosin), wool	F. Orange-yellow S. Bright yellow	Slowly decolorised	F. Light yellow S. —
Erythrosin, wool	F. Orange-red, becoming yellow-brown S. —	Orange-yellow	F. Orange-yellow S. —
Safrosin, wool	F. Dirty green-yellow S. Yellow	Slowly decolorised	F. Nearly decolorised S. —
Phloxin, wool	F. Bright orange, becoming brown-yellow S. —	Slowly decolorised	F. Dull yellow S. —
Cyanosin, wool	F. Bright orange, becoming brown-yellow S. —	Redder	F. Orange-red S. —
Rose Bengal, wool	F. Reddish brown S. —	Slowly decolorised	F. Decolorised S. —
Rose Bengal B, wool	F. Bright orange; becoming orange, and finally dirty yellow S. Reddish yellow	Slowly decolorised	F. Decolorised S. —
Cyclamin, wool	F. Reddish brown S. Brown	Decolorised	F. Flesh coloured S. —

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
...	Dirty yellow, with blue border	F. Red-violet S. Faint violet	F. Reddish violet S. Faint violet	Slowly decolorised
...	Yellow, with blue border	F. Dull crimson S. —	F. Brownish maroon S. —	...
F. Cinnabar-red S. —	F. Brick-red, then yellow S. Yellowish	F. — S. Rose	F. More brownish S. —	...
...	Yellowish orange	F. Bright scarlet S. Red	F. Reddish violet S. Dirty violet	Rapidly decolorised
...	Dull red	F. Orange-red S. Orange	F. Cherry-red S. —	Slowly decolorised
Fades slightly	Yellow-red	Fades to red	Fades to red	Colourless
...	Orange-red	F. Little change S. —	F. Redder S. —	...
...	Red-orange	F. Crimson S. Pale rose	F. Crimson S. Light red	Yellow
...	F. Yellower S. Pale scarlet	...	F. Yellower* S. Orange-yellow	Pale bluish crimson
...	Yellow	F. Decolorised S. —	F. Decolorised S. —	Little change
...	...	F. Bluer S. Rose	F. Maroon S. —	...
...	Yellow	F. Brighter S. Rose	F. Brighter S. Rose	Orange-yellow
...	Bright yellow	F. Brighter S. Rose	F. Darker S. Rose	Decolorised
...	Yellow	F. Little change S. Rose	F. Little change S. Rose	Orange-yellow
...	Yellow	F. Darker S. Rose	F. Darker, becom- ing orange-red S. —	Decolorised
...	Yellow	F. Little change S. Rose	F. Little change S. Rose	Decolorised
...	Yellow, with orange border	F. Little change S. Rose	F. Little change S. Rose	Bright orange-red
...	Yellow	F. No change S. Rose	F. Rather darker S. —	Decolorised
...	Yellow	F. Darker S. Rose	F. Darker S. —	Decolorised
...	Yellow	F. — S. Rose	...	Decolorised

\* With 5 per cent. NaOH.

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Rhodamine B, wool	F. Yellow; colour restored on dilution S. Yellow; rose on dilution	Brighter	F. Orange; colour restored on dilution S. —
Rhodamine 3B, wool	F. Yellow; bright rose on dilution S. Yellow; bright rose on dilution	Brighter	F. Orange; colour restored on dilution S. —
XL Acid eosin 3B, wool (R)	F. Dark crimson S. —	...	F. Dark crimson; colour restored on dilution S. Rose on dilution
Rosinduline 2G, wool	Dark green	Slight change	Brown-yellow
Eosamin B, wool	Blue-black	Slight change	Violet
Apollo red, wool	Red-violet	Slight change	Violet
Chromotrope 2R, wool	Darker	No change	Fainter
Chromazone red, wool	Blue-black	No change	More violet
Lanafuchsin, wool	F. No change S. Magenta-red	No change	F. No change S. Reddish
Lanafuchsin BBS (C)	F. Blue S. Blue	...	F. Brownish red S. Colourless
Fast acid eosin, wool	Pale yellow	No change	Yellow
Azo carmin G, wool	Dark green	Browner, fading to yellow	Dirty green
Azo acid carmin B, wool	F. Dark blue S. Brown	Faint violet	F. Red S. Red
Guinea carmin B, wool	F. Violet S. Blue	No change	F. Very slightly violet S. Violet-red [let
Anthracene red, wool	F. Bluish crimson; pale red on dilution F. Bluish crimson; pale red on dilution	...	F. Much darker S. —
Salicin red, on wool mordanted with chromium fluoride	F. Becomes tinged with blue S. Violet-red	No change	F. Slight change S. Slightly red
Salicin red B, wool	F. — S. Violet-red	No change	Red-brown
Salicin red 2G, on wool mordanted with chromium fluoride	F. Carmine-red S. Carmine-red	No change	F. Carmine-red S. Carmine-red
Salicin red 2G, wool	F. Carmine-red S. Carmine-red	No change	F. Red-brown S. Slightly red
Chrome fast red B (direct colour), wool	F. Black S. Blue; red-violet on dilution	F. Brown S. —	F. Black-brown S. —
Chrome fast red B, on wool subsequently treated with chromium fluoride	F. Black S. Blue; red-violet on dilution	F. Brown S. —	F. Black-brown S. —

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
...	Yellow	F. Rather bluer S. Colourless	F. Bluer S. Colourless	Brighter
...	Red	F. Rather bluer S. —	F. Rather bluer S. —	Scarlet
...	F. Dark crimson S. —	F. Yellow-red S. Yellow-red	F. Yellow-red S. Yellow-red	...
Slight change	Yellow	Slight change	Slight change	Brown
Slight change	Brown-red	Slight change	Browner	Brighter
Slight change	Red	Brighter	Browner	Darker
No change	Yellow	More violet	Yellowish	Slowly paler
No change	Brown-yellow	More violet	Brown-red	Paler
No change	Yellow	Brownish	Red-brown	Decolorised
...	F. Bright red S. Pale red	...	F. Brownish red * S. Pale red	Decolorised
No change	Light yellow	Yellowish	Dirty rose	Orange
Browner, fading to yellow	Red	Fades to red	Fades to red	Darker, fades to violet
No change	Dark yellow	F. Slight change S. Slightly red	Dark red	Decolorised
No change	Yellow	F. Slight change S. Slightly red	Brown-red	Slowly decolorised
...	Orange	F. — S. Pale rose	F. — S. Orange-red	Decolorised
No change	Orange	No change	Red-brown	Nearly decolorised
Slightly reddish	Orange	No change	Red-brown	Nearly decolorised
No change	Yellow	No change	Brown	Decolorised
No change	Yellow	F. No change S. Slightly reddish	Red-brown	Decolorised
F. Dark brown S. —	F. Dark brown S. Yellow-brown	F. Slightly red- brown S. Reddish	F. Dark brown S. Red-brown	F. Dark brown S. —
F. Dark brown S. —	F. Black-brown S. Yellow-brown	F. Slightly red- brown S. Rather reddish	F. Dark brown S. Brown-red	F. Dark brown S. —

\* With 5 per cent. NaOH.



Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Chrome fast red B, on wool subsequently treated with potassium bichromate	F. Black S. Blue; red-violet on dilution	F. Brown S. —	F. Black S. —
Chrome fast red G (direct colour), wool	F. Dark brown S. Red-violet; light brown on dilution	F. Unchanged S. —	F. Dark brown S. Slightly reddish violet
Chrome fast red G, on wool subsequently treated with chromium fluoride	F. Dark brown S. Reddish violet; red-dish brown on dilution	F. Brown S. —	F. Black-brown S. —
Chrome fast red G, on wool subsequently treated with potassium bichromate	F. Dark brown S. Violet; brown-yellow on dilution	F. Little change S. —	F. Dark brown S. —
Chrome fast red R (direct colour), wool	F. Black-brown S. Blue-violet; on dilution reddish violet	F. Brownish S. —	F. Dark brown S. —
Chrome fast red R, on wool subsequently treated with chromium fluoride	F. Black-brown S. Blue-violet; on dilution red-violet	F. Brown S. —	F. Black-brown S. —
Chrome fast red R, on wool subsequently treated with potassium bichromate	F. Black-brown S. Blue-violet; red-brown on dilution	F. Dark brown S. —	F. Black-brown S. —
Fast acid phloxin A, silk	F. Yellowish, nearly decolourised; colour restored on dilution S. —	F. Unchanged S. —	F. Yellowish; colour restored on dilution S. —
Acid rhodamine 3R, silk	F. Orange S. —	F. Unchanged S. —	F. Orange S. —
Rhodamine 6G, cotton	F. Yellow; rose on dilution S. Yellow; rose on dilution	Lighter	F. Orange-yellow; rose on dilution S. —
Rhodine BS, on tannin-mordanted cotton (BF)	F. Orange S. Orange on dilution	...	F. Brick-red, then orange S. —
Rhodine 3G, on tannin-mordanted cotton (BF)	F. Orange-yellow S. Reddish orange on dilution	...	F. Brick-red, then orange S. —
Rhodamine S, cotton	F. Yellow; rose on dilution S. Yellow; rose on dilution	Lighter	F. Orange-yellow; rose on dilution S. —
Magenta, wool and cotton	F. Brownish yellow S. Yellow	F. Darker and bluer S. Colourless	F. Yellow S. Slightly yellow
New magenta, wool and cotton	F. Yellow S. Yellow	F. Dark maroon, becoming brown S. Colourless	F. Yellow S. Slightly yellow
Safranine, wool and cotton	F. Dark green S. Light green	F. Bluer S. Colourless	F. Dark blue S. Blue

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
F. Dark brown S. —	F. Black-brown S. Yellow-brown	F. Faint brownish S. —	F. Dark brown S. Red-brown	F. Dark brown S. —
F. Light brown- ish S. —	F. Yellow-brown S. Faint reddish brown	F. Unchanged S. Slightly reddish	F. Brown-yellow S. Brown-yellow	F. Red-brown, slowly becomes decolor- ised S. Colourless
F. Dark brown S. —	F. Black-brown S. Faint reddish ; brownish on dilution	F. Unchanged S. —	F. Brown S. Brown-yellow	F. Dark brown S. —
F. Dark brown S. —	F. Dark brown S. Reddish brown	F. Unchanged S. —	F. Brown S. Yellowish brown	F. Dark brown, slowly becoming lighter brown S. —
F. Dark brown S. —	F. Dark brown S. Reddish brown	F. Brown-red S. Slightly reddish	F. Dark brown S. Yellowish brown	F. Dark brown S. —
F. Brown S. —	F. Dark brown S. Yellowish red	F. Brown-red S. —	F. Brown S. Red-brown	F. Black-brown S. —
F. Dark brown S. —	F. Black-brown S. Yellow-red	F. Unchanged S. —	F. Brown S. Brown-red	F. Black-brown S. —
F. Unchanged S. —	F. Yellow S. —	F. Unchanged S. —	F. Unchanged S. —	F. Rather paler rose S. —
F. Unchanged S. —	F. Yellow S. —	F. Rather more bluish red S. —	F. Rather more bluish red S. —	F. Little change S. —
...	F. Orange S. Rose	F. Little change S. —	F. Yellower S. Light red	Lighter
...	F. Brownish red S. Rose	...	F. More tinged with red S. —	F. More tinged with red S. —
...	F. Carmine S. Rose	...	F. Yellowish red S. —	F. Slowly becomes pale orange S. —
...	Orange-red	F. Little change S. Rose	F. Lighter S. —	Lighter
...	Yellow	F. Slowly decolor- ised S. —	F. Nearly decolor- ised S. —	Slowly decolorised
...	Bright yellow	F. Slowly decolor- ised S. —	F. Nearly decolor- ised S. —	Slowly decolorised
...	First red-blue, then green, finally yellow	F. No change S. —	F. No change S. —	Decolorised on warm- ing

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Pyronine G, cotton	Yellow	Slight change	Orange
Induline scarlet, cotton	Brown-red	No change	Green
Congo red, cotton	F. Deep blue S. Blue	Blue	F. Blue S. Colourless
Congo red 4R, cotton	F. Deep blue S. Blue	Dull purple	F. Deep blue S. Colourless
Brilliant Congo R, cotton	F. Deep blue S. Blue	Duller	F. Olive-brown S. Colourless
Benzopurpurine B, cotton	F. Deep green-blue S. Blue	Dull red	F. Olive S. Colourless
Benzopurpurine 4B, cotton	F. Deep blue S. Blue	Dark slate	F. Bright blue S. Colourless
Benzopurpurine 10B, cotton	F. Indigo-blue S. Blue	Blue	F. Blue S. Colourless
Brilliant purpurine R, cotton	F. Deep blue S. Blue	Dull violet	F. Dull blue S. Colourless
Delta purpurine 5B, cotton	F. Deep bright blue S. Blue	Reddish brown	F. Brown-olive S. Colourless
Delta purpurine 7B, cotton	F. Deep green-blue S. Blue	Browner	F. Brown S. Colourless
Columbia fast red F, cotton (A)	F. Blue-black S. Dirty violet	F. Brown S. —	F. Violet-black S. —
Rosazurine, cotton	F. Deep green-blue S. Green-blue	Browner	F. Brown-olive S. Colourless
Diamine red NO, cotton	F. Deep blue S. Blue	Dull violet	F. Olive S. Colourless
Diamine scarlet B, cotton	F. Blue-violet S. Violet	Little change	F. Violet S. Violet
Diamine fast red F, cotton	F. Deep red-blue S. Blue	Duller	F. Red-violet S. Colourless
Thiazin red R, cotton	Brown-red	Slight change	Violet-red
Thiazin red G, cotton	Magenta-red	Slight change	Magenta-red
Sorbin red, cotton	Brighter	Slight change	Fades to red, and becomes rather browner
Glycine red, cotton	Blue-black	Blue	Blue
Brilliant geranin B, cotton	Blue-green	Darker	Violet
Diamine rose BD, cotton	F. Violet-red S. Violet-red	No change	F. No change S. Slightly violet-red
Hessian purple N, cotton	F. Green-blue S. Green-blue	Dull violet	F. Blue-violet S. Colourless
Hessian brilliant purple, cotton	F. Blue S. Blue	Little change	F. Grey S. Colourless
Naphthylene red, cotton	F. Dull blue S. Blue	Dull violet	F. Dark blue-green S. Colourless

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
Slight change	Red	Fainter	Almost colourless	Orange
No change	Brown-yellow	Darker	Darker	Pale violet
...	Blue	F. No change S. —	F. No change S. —	Decolorised
...	Orange	F. Little change S. Rose	F. Little change S. —	Decolorised
...	Light red	F. No change S. —	F. Rather yellower S. —	Decolorised
...	Light brown	F. Little change S. Rose	F. Yellower S. —	Decolorised
...	Yellow	F. Little change S. —	F. Little change S. —	Decolorised
...	Yellow	F. Little change S. —	F. Little change S. —	Decolorised
...	Yellow	F. No change S. Slightly rose	F. No change S. —	Decolorised
...	Yellow	F. No change S. —	F. No change S. —	Decolorised
...	Light brown	F. Little change S. Rose	F. Little change S. —	Decolorised
F. Brown-black S. —	F. Dark brown S. Yellow	F. Rather deeper S. —	F. Deeper S. —	Blue-violet
...	Light brown	F. No change S. —	F. Little change S. —	Decolorised
...	Light brown	F. Little change S. Rose	F. Little change S. —	Decolorised
...	Crimson	F. Orange S. —	F. Orange S. —	Decolorised
...	Brown	F. Little change S. —	F. Brown S. —	At first dull purple, then slowly decolorised
Slight change	Red	Violet	Violet	Colourless
Slight change	Magenta-red	Darker	Darker	Colourless
Slight change	Yellow-brown	Slight change	Brown	Slight change
Blue	Fades dirty yellow- green; fibre green- grey	Bright red	Bright red	Colourless
Darker	Violet	More violet	More violet	Colourless
No change	Orange	Slightly violet	Slightly violet	Decolorised
...	Brown	F. Rather redder S. Rose	F. Little change S. —	Decolorised
...	Brown	F. Little change S. —	F. Little change S. —	Decolorised
...	Olive-green	F. Little change S. —	F. Little change S. —	Decolorised

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Rosopenin 4 B } cotton St Denis red }	F. Dark crimson S. Crimson	Little change	F. Blue S. Colourless
Rosanthren B, on cotton diazotised and coupled with $\beta$ -naphthol after dyeing (J)	F. Black S. Rose on dilution	F. Rather darker S. —	F. Dark carmine S. —
Rosanthren R, on cotton diazotised and coupled with $\beta$ -naphthol after dyeing (J)	F. Dark carmine S. Yellowish red on dilution	F. Rather darker S. —	F. Carmine S. —
Rosanthren AW (I)	F. Bluish purple S. Bluish purple	...	F. Purple S. Colourless
Rosanthren GW (I)	F. Crimson S. Crimson	...	F. Crimson S. Colourless
Rosanthren RW (I)	F. Crimson S. Crimson	...	F. Bluish crimson S. Colourless
Rosanthren pink (I)	F. Deep blue S. Bright azure-blue	...	F. Purple S. Colourless
Erika B (cotton) }	F. Purple S. Violet	Redder	F. Redder S. Colourless
Geranin 2B, cotton	F. Crimson S. Rose	Little change	F. Little change S. —
Paranitraniline red, cotton	F. Deep magenta - red ; orange-red on dilution S. Magenta-red ; orange- red on dilution	No change	F. Little change S. —
Thiogen rubin O (M)	F. Bluish purple S. Colourless	...	F. Purplish blue S. Colourless
Thioindigo red B (K)	F. Duller and bluer S. Colourless	...	No change
Algol red B (By.)	F. Bluish purple S. Purple	...	F. Redder S. Colourless
Vat red (B)	F. Red S. Colourless	...	F. Maroon S. Colourless
Ciba scarlet G (I)	F. No change S. Colourless	...	F. No change S. Colourless
Algol scarlet G (By.)	F. No change S. Keddish	...	F. No change S. Colourless
Algol Bordeaux 8B (By.)	F. Little change S. Maroon	...	F. Little change S. Colourless
<b>Brown Dyes</b>			
Anthracene brown on chromed wool	F. Redder S. Brown	No change	F. Yellower S. Light brown
Cloth brown (reddish) on chromed wool	F. Very dark violet S. Violet	Much darker	F. Dark violet S. —
Gambin on chromed wool	F. Dark brown S. Light brown	Redder	F. Little change S. —

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
...	Little change <sup>c</sup>	F. Orange-red S. Orange-red	F. Orange-red S. Light orange	Decolorised
F. Darker S. —	F. Brownish red S. —	F. Rather lighter S. —	F. Rather more yellowish S. —	F. Dark carmine S. —
F. Rather darker S. —	F. Reddish brown S. —	F. Rather lighter S. —	F. Rather darker S. —	F. Carmine S. —
...	F. Bluish crimson S. Colourless	...	No change *	Little paler
...	F. Orange-brown S. Yellowish	...	F. Yellower * S. Colourless	No change
...	F. Orange S. Pale yellow	...	No change *	No change
...	F. Purplish brown S. Colourless	...	F. Brownish purple * S. Colourless	Pale bluish pink
...	Pale red	F. Little change S. Rose	F. Rather bluer S. Colourless	Slowly decolorised
...	Little change	F. Violet S. Violet	F. Violet S. —	Decolorised
...	F. Crimson S. Scarlet	F. Little change S. —	F. Dark brick-red S. —	Decolorised
...	F. Pale dull crim- son S. Colourless	...	No change *	Bluer
...	No change	...	No change *	No change
...	F. Paler and redder S. Pale red	...	No change *	Little change
...	F. Red S. Colourless	...	F. Red * S. Colourless	F. Red S. Colourless
...	F. No change S. Colourless	...	F. No change * S. Colourless	No change
...	F. Orange S. Orange	...	F. No change * S. Colourless	F. No change S. Colourless
...	F. Yellow S. Yellow	...	F. No change * S. Colourless	No change
...	Dark orange	F. Olive to black S. Colourless	F. Olive to black S. Colourless	Little change
...	Dark red, with dark violet border	F. Darker S. —	F. Darker S. —	Little change
...	Brownish yellow	F. Little change S. —	F. Yellower S. Pale yellow	Redder

\* With 5 per cent. NaOH.

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Dioxin on chromed wool	F. Dark green S. Green	Little change	F. Darker S. Light brown
Anthracene acid brown B, on chromed wool	F. Violet-red S. Violet-red	No change	F. Darker S. Faint violet-red
Anthracene acid brown B, wool	F. Violet-red S. Violet-red	No change	F. Reddish S. Violet-red
Janus brown B, cotton, wool, silk	Grey-black	No change	Brown-black
Janus brown R, cotton, wool, silk	Blue-black	No change	Blue-black
Domingo chrome brown B, on wool subsequently treated with potassium bichromate (L)	F. Black S. —	...	F. Black S. —
Domingo alizarin brown G, on wool subsequently treated with potassium bichromate (L)	F. Dark brown S. —	...	F. Darker S. —
Palatine chrome brown R (B)	F. Bluish crimson S. Crimson tint	...	F. Bluish crimson S. Colourless
Anthracene chrome brown SWN (C)	F. No change S. Colourless	...	F. Dark red S. Faint red
Anthracene chromate brown 3G (C)	F. Lighter S. Colourless	...	F. Dark brown S. Brownish tinge
Anthracene chromate brown EB (C)	F. No change S. Colourless	...	F. Little lighter S. Pink
Pegu brown, silk	Cherry-red	No change	Brown-red
Alizarin brown G, wool	Blue	Slight change; browner	F. Black S. Reddish
Alizarin red-brown R, wool	Black, solution brown-red	No change	F. Black S. Black brownish red
Fast brown (MLB), wool	F. Blue S. Blue	No change	F. Dark crimson S. Rose
Naphthylamine brown, wool	F. Bright blue S. Blue	No change	F. Darker S. Blue
Fast brown (Bayer), wool	F. Red-violet S. Red-violet	No change	F. Dark maroon S. Rose
Fast brown G, wool	F. Dirty brown S. Red	F. Darker S. Brown	F. Chocolate-brown S. —
Fast brown 3B, wool	F. Dark blue S. Red-blue	...	F. Violet S. Slightly violet
Acid brown G, wool	F. Dirty purple S. Purple	Brighter	F. Darker S. Slightly yellow
Acid brown R, wool	F. Dark violet S. Violet	No change	F. Dark violet S. Violet

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
...	...	F. Dark green S. Faint red	F. Very dark green S. —	...
No change	Dark yellow-brown	No change	F. Slightly reddish S. Slightly reddish	Yellow-green
No change	Yellow-brown	F. Slight change S. Brownish	F. Red-brown S. Red-brown	Grey
No change	Dirty brown	Fades to pale red	No change	Brown-yellow, almost colourless
No change	Cotton: blue-black, then red-brown Wool: blue-black, then brown-yellow Silk: blue-black, then grey-black	Fades slightly	Fades slightly to brownish red	Cotton: yellowish, almost colourless Wool: brown-red Silk: brown-red
...	F. Black, then yellow-brown S. —	F. Darker S. —	...	...
...	F. Dark brown, slowly paler S. —	F. Rather paler S. —	F. Pale reddish brown S. —	...
...	F. Crimson, then yellowish red S. Yellow tint	...	F. Redder * S. Colourless	Little change
...	F. Reddish brown S. Brown	...	F. No change * S. Colourless	Decolorised
...	F. Lighter S. Yellow tinge	...	F. Little darker * S. Brown tinge	Decolorised
...	F. Much lighter S. Dark brown	...	F. No change * S. Colourless	F. Light red S. Light red
No change	Brownish red	No change	No change	Yellowish
Slight change; brownier	F. Black S. Red-brown	Brown-red	Brown-red	Brown: slowly de- colorised
No change	Yellow	Rather redder	F. Darker S. Red	Slowly becomes paler
...	Yellow, with scarlet border	F. Darker S. —	F. Darker S. —	...
...	Dirty yellow, with maroon border	F. Crimson S. Crimson	F. Bluish crimson S. Colourless	Little change
...	Yellow, with maroon border	F. Yellower S. Yellow-brown	F. Dull scarlet S. —	Paler
...	Yellow, with maroon border	...	...	Paler
...	Yellow, with orange border	F. Crimson S. Rose	F. Crimson S. —	Bluer
...	Dirty yellow, with pale maroon border	F. Brighter S. Faint brown	F. Rather darker S. —	Little change
...	Greenish yellow, with purple border	F. Scarlet S. Rose	F. Bright scarlet S. —	Nearly decolorised

\* With 5 per cent. NaOH.



Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Bismarck brown GG, wool	F. Purple; colour restored on dilution S. Red-brown	F. Darker S. Colourless	F. Maroon S. Red
Benzo brown G, cotton	F. Darker S. Grey	No change	F. Dark brown S. Light brown
Benzo brown B, cotton	F. Dark purple S. —	Darker	F. Darker S. Light brown
Benzo brown NBR, cotton	F. Dark blue S. Dull blue	Bluer	F. Red-violet S. Colourless
Benzo brown 5R (Terra-cotta F, Alkali brown (Dahl), Cotton brown R), cotton	F. Crimson S. Crimson	Little change	F. Little change S. Rose
Terra-cotta F	Dark red	Slight change	Red
Columbia brown M, cotton (A)	F. Brown-black S. Brown	F. Red-brown S. —	F. Violet-black S. —
Benzo black-brown, cotton	F. Grey-black S. Brown on dilution	Little change	F. Dark violet; colour restored on dilution S. —
Congo brown G, cotton	F. Dark violet S. Violet	Little change	F. Violet S. Colourless
Congo brown R, cotton	F. Violet S. —	Yellower	F. Blue-violet S. —
Hessian brown 2B, cotton	F. Dirty blue-violet S. —	Duller	F. Discoloured S. —
Mikado brown, cotton	F. Violet S. Violet	Yellow	F. Brown S. Colourless
Tolylene brown, cotton	F. Dark violet S. Violet	Greener	F. Darker S. Rose
Cotton brown A, cotton	F. Dark green S. —	Little change	F. Darker S. Colourless
Cotton brown N, cotton	F. Blue-black S. Grey	Darker	F. Darker S. Light brown
Diamine brown V, cotton	F. Dark red-blue S. Red-blue	No change	F. Little change S. —
Diamine brown R, cotton	F. Violet S. Violet	...	Sp. gr. 1.16 F. Black S. —
Diamine bronze, cotton	Blue	No change	Violet-red
Diazo brown R extra, cotton	Violet-black	No change	Fades to reddish
Direct brown N, cotton (L)	F. Dark red-brown S. —	...	F. Dark brown S. Red; yellow on dilution
Direct brown OOO (direct colour), cotton (L)	F. Blue-black S. —	F. Dark brown S. —	F. Violet-black S. —
Benzonitrol brown 2R, cotton	Violet	Slight change	Slight change

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
...	...	F. Little change S. —	F. Browner S. —	Paler
...	Darker	F. Little change S. Faint orange	F. Little change S. —	Paler
...	Darker	F. Little change S. Faint brown	F. Little change S. —	Paler
...	Little change	F. Redder S. Rose	F. Redder S. —	Paler
...	Yellow-brown	F. No change S. —	F. Little change S. —	Slowly decolorised
No change	Brown-red	Slight change	Slight change	Slowly decolorising
...	F. Violet-black S. Pale violet	F. Rather deeper S. —	F. Dark red-brown S. Rose	F. Red, tinged with S. yellow
...	Red-orange	F. Little change S. —	F. Darker and red- der —	Nearly decolorised
...	Dark violet	F. Redder S. —	F. Crimson S. Crimson	Decolorised
...	Red-violet	F. Paler S. —	F. Crimson S. —	Decolorised
...	...	F. Little change S. —	F. Little change S. —	Decolorised
...	Olive	F. No change S. —	F. Little change S. —	Decolorised
...	Brown	F. No change S. —	F. Little change S. —	Decolorised
...	Little change	F. No change S. —	F. No change S. —	Decolorised
...	Darker	F. Little change S. Pale orange	F. Little change S. —	Paler
...	Dull violet	F. Little change S. —	F. Little change S. Rose	Nearly decolorised
...	Sp. gr. 1.42 F. Decolorised S. Pale red	...	Fibre and solution red on warming	Violet in the cold; decolorised on warming
No change	Brown-red	Darker	Browner	Colourless
No change	Dirty brown-red	Slight change	Slight change	Rapidly becomes faint yellow
...	F. Yellow-brown S. Yellow	...	...	F. Flesh-coloured S. —
F. Dark brown S. —	F. Violet-black S. —	F. More tinged with red —	F. Rather deeper and more tinged with red S. —	F. At first dark brown, then red- dish orange S. —
No change	Brown-red	Slight change	Slight change	Slowly becomes yellow

Dyestuff.	Concentrated Sulphuric Acid.	10 per cent. Sulphuric Acid.	Concentrated Hydrochloric Acid.
Benzonitrol dark brown N, cotton	Violet	Slight change	Slight change
Oxamine maroon, cotton	Blue	Slight change	Blue
Pluto brown R, cotton	Violet	No change	Darker
Thiazin brown G, cotton	Brown-red	No change	Brown
Thiazin brown R, cotton	Red	No change	Brown
Diphenyl brown, cotton	Blue	Redder	Violet
Diamine nitrazol brown, cotton	F. Dark red S. Dark carmine-red	No change	Reddish
Indanthren copper R (B)	F. Little lighter S. Light red	...	F. Yellow S. Colourless
Indanthren brown B (B)	F. No change S. Colourless	...	F. No change S. Colourless
Thiocatechin I, cotton	Browner	No change	Darker
Thiocatechin S, cotton	Brighter	No change	Slight change
Sulphur catechu R, cotton (A)	F. Little change S. —	F. Rather darker S. —	F. Rather darker S. Reddish
Sulphur catechu G, cotton (A)	F. Little change S. —	F. Rather darker S. —	F. Little change F. Very slightly reddish
Immedial catechu O, cotton (C)	F. Yellow-brown S. —	...	...
Immedial Bordeaux G (C)	F. Black S. Dull purple	...	F. Paler and redder S. Colourless
Immedial dark brown D (C)	F. Little change S. Yellowish brown	...	No change
Immedial prune S (C)	F. Darker S. Greyish purple	...	F. Little redder S. Colourless
Sulphur brown G, cotton	F. Dark yellow-brown S. Slightly yellowish brown	F. Unchanged S. —	F. Yellowish brown S. —
Sulphur brown 2G, cotton	F. Yellow-brown S. Brownish	F. Unchanged S. —	F. Paler yellowish brown S. —
Pyrogen brown D, cotton	F. Black S. —	F. Rather darker S. —	F. Darker S. —
Pyrogen brown M, cotton	F. Rather darker S. Brown	F. Unchanged S. —	F. Unchanged S. —
Pyrrrol brown G, cotton (L)	F. Paler S. Light brown on dilution	...	F. Paler S. —

10 per cent. Hydrochloric Acid.	Nitric Acid. Sp. gr. 1.40.	Ammonium Hydroxide. Sp. gr. 0.91.	10 per cent. Sodium Hydroxide.	Stannous Chloride and Hydrochloric Acid.
No change	Brown - red ; fibre rather lighter	No change	Slight change	Slowly becomes yellow
No change	Violet	No change	Fades to reddish	Colourless
No change	Brown-red	Redder	Redder	Colourless
No change	Brown-red	Redder ; fades to yellow	Redder	Pale yellowish
No change	Brown-red	Redder ; fades to yellow	Redder	Pale yellowish
Redder	Violet	Darker	Browner	Colourless
No change*	Brown	Reddish	Reddish	Light yellow
...	F. Yellow S. Light yellow	...	F. No change* S. Colourless	F. Yellow S. Colourless
...	F. No change S. Colourless	...	F. No change* S. Colourless	F. No change S. Colourless
No change	Yellow-red	Darker	Dark brown	Dirty brown ; darker
No change	Yellow	Darker	Rather fainter	Almost colourless
F. Unchanged S. —	F. Little change S. —	F. Rather paler S. —	F. Rather paler S. —	F. Unchanged S. —
F. Unchanged S. —	F. Little change S. —	F. Rather paler S. —	F. Rather paler S. —	F. Rather paler S. —
...	F. Dark brown S. —	...	...	...
...	F. Dull orange S. Dull orange	...	F. Yellowish brown* S. Colourless	F. Dull purple S. Colourless
...	F. Little change S. Dull yellow	...	No change*	Little change
...	F. Orange-brown S. Brown	...	F. Reddish brown* S. Colourless	Lighter
F. Unchanged S. —	F. Yellowish brown S. Slightly brown	F. Unchanged S. —	F. Unchanged S. —	F. Pale yellow-brown S. —
F. Unchanged S. —	F. Yellow-brown S. Slightly yellow- ish	F. Unchanged S. —	F. Rather paler yel- low-brown S. —	F. Light brown S. —
F. Darker S. —	F. Darker S. —	F. Little change S. —	F. Little change S. —	F. Little change S. —
F. Unchanged S. —	F. Lighter brown S. Slightly yellow- ish	F. Unchanged S. Unchanged	F. Unchanged S. —	F. Unchanged ; after some time rather paler S. —
...	F. Rather darker S. —	...	F. Rather lighter S. —	F. Rather lighter S. —

\* With 5 per cent. NaOH.

A. Meienberg<sup>1</sup> recommends the following reactions for the examination of a few sulphur dyestuffs and of aniline black:—

	Alkaline Sodium Peroxide.	Concentrated Sulphuric acid.	Hyposulphite.	Stannous Chloride and Hydrochloric acid.	After the preceding test the washed fibre is warmed with dilute Ammonium Hydroxide.
Immedial black V	S. Nearly colourless F. Blue	S. Violet-black F. Easily soluble	All light brown; the colour is completely restored on washing.	F. Light brown; after washing, violet- black	S. Violet.
Immedial black G	S. Dirty green F. Blue	S. Blackish violet F. Easily soluble		F. Dark brown; after washing, brown- black	S. Nearly colour- less.
Immedial black FF	S. Nearly colourless F. Blue	S. Violet-black to bluish violet F. Easily soluble		F. Light brown; after washing, violet- black	S. Pale violet.
Vidal black (old)	S. Light green F. Green, much lighter	S. Olive-black F. Sparingly soluble		F. Dark brown; after washing, dark olive-yellow	S. Nearly colour- less.
St Denis black	S. Light green F. Olive-green, nearly decolorised	S. Olive-black F. Sparingly soluble		F. Dark brown; after washing, olive coloured	S. Blackish blue.
Half-wool black	S. Dull greenish blue F. Light green, nearly decolorised	S. Dull violet-black F. Sparingly soluble		F. Light brown; after washing, dark olive coloured	S. Blue.
Catigen black	S. Nearly colourless F. Unchanged	S. Dull violet-black F. Sparingly soluble		F. Light brown; after washing, black	S. Colourless.
Sulphur black T	S. Nearly colourless F. Unchanged	S. Greenish black F. Sparingly soluble		F. Light brown; after washing, black	S. Colourless.
Sulphaniline black G	S. Colourless F. Blue	S. Violet-black F. Easily soluble		F. Light brown; after washing, violet- black	S. Violet.
Eclipse Black B	S. Pale bluish green F. Blue and paler	S. Blue-black F. Sparingly soluble		F. Light brown; after washing, olive- black	S. Blue.
Clayton fast black BM	S. Pale blackish F. Rather brighter	S. Black F. Slightly soluble		F. Dark brown; after washing, dark brown	S. Nearly colour- less.
Aniline black <sup>2</sup>	S. Pale brownish F. Brownish	Brownish black		F. Brownish black; after washing, blackish purple	S. Colourless.

<sup>1</sup> *J. Soc. Dyers and Col.*, 1901, 17, 61.

<sup>2</sup> *Cf.* also *Aniline Black*, by E. Nölting and A. Lehne, 1904, p. 159.

C. H. Whittaker<sup>1</sup> gives the following instructions for the examination of black-dyed cotton. The black shades produced by substantive dyestuffs by direct dyeing, bleed freely when they are treated with boiling water.

Logwood black can be very easily recognised by the fact that it is removed from the fibre by warming with dilute hydrochloric acid or sulphuric acid, whereby the acid solution acquires an orange-red to red colour whilst the cotton itself becomes purple to reddish brown; an excess of sodium hydroxide makes the acid solution more violet.

The black colours obtained by diazotising azo dyestuffs on the fibre and coupling with  $\beta$ -naphthol or similar substances are destroyed completely by boiling with sodium hyposulphite; aniline black and blacks derived from sulphur dyestuffs are only temporarily decolorised by this treatment, the original colour being restored on washing with water.

The differentiation of aniline black, sulphur black, and sulphur black topped with aniline black can be effected as follows:—

A solution of calcium hypochlorite (sp. gr. 1.022) is heated to boiling and the samples under examination are placed in it. Aniline black becomes nut-brown, a sulphur black topped with aniline black is turned yellow to light brown, whilst sulphur black itself is completely bleached.

If the cotton is placed in concentrated sulphuric acid and, after the fibre has become carbonised, the solution is diluted somewhat with water, a pale green solution denotes the presence of aniline black and a colourless solution the presence of sulphur dyestuffs.

In extension of the preceding, F. Neurath<sup>2</sup> remarks as follows concerning the reactions of black sulphur dyestuffs, which should be tried unless the black has been ascertained to be produced by direct dyeing with a substantive azo dyestuff.

The dyed cotton is boiled with dilute sodium hydroxide. The formation of a greyish blue to steel-blue colour in the alkaline solution indicates the presence of a sulphur black.

When the skein is plaited with white cotton and boiled with sodium sulphide, the white cotton becomes dyed. This property of bleeding by boiling with sodium sulphide is exhibited by all sulphur dyestuffs. In the case of most of the blue sulphur dyestuffs, however, the dyestuff is converted into its leuco compound; if this is poured on filter-paper, the blue colour is restored after a short time.

### The Spectroscopic Examination of Dyestuffs.

It is well known that when white light falls on a solution of a dyestuff, one portion of the coloured rays constituting the white light is absorbed whilst another portion is transmitted. Also, the same rays are absorbed if the white light has been first resolved into its con-

<sup>1</sup> *J. Soc. Dyers and Col.*, 1902, 18, 172.

<sup>2</sup> *Ibid.*, 1902, 1, 579.

stituents by passage through a prism; these rays are missing, therefore, in the spectrum, more or less sharply defined dark bands appearing in their place. The intensity and the breadth of the latter depend greatly on the concentration of the solution of the dyestuff and also on the thickness of the layer.

The absorption manifests itself chiefly in the colour complementary to that of the dyestuff. For example, a dilute solution of magenta shows a black band in the yellow green, all other colours being transmitted or only slightly weakened. In more concentrated solutions the band becomes broadened in the direction of the blue, so that this and finally also the violet are absorbed. The absorption bands of many dyestuffs are sufficiently characteristic for their identification after a little experience. Great experience is necessary, however, in order to be able to use the spectroscope successfully. To all intents and purposes the spectroscope is only a more sensitive eye, and standards of comparison should always be utilised to prevent the occurrence at times of very serious errors. The pocket spectroscope, first constructed by John Browning of London, answers quite well for the spectroscopic examination of dyestuffs. The provision of a comparison prism for the same is highly desirable, since otherwise it is difficult to locate the position of the absorption bands.

The pocket spectroscope has the great advantage of direct vision. For greater convenience of manipulation H. Vögel has constructed a very practical stand. When the latter is not available, the spectroscope can be fixed in an ordinary burette clamp with the slit directed towards a window, and the liquids under examination are placed in test-tubes or, better, bottles with parallel walls held in front of the slit. The slit and lens are so adjusted that the Fraunhofer lines appear sharp and distinct in diffused daylight. The comparison prism is also arranged so that the field of view consists apparently of only one spectrum separated into two equal halves by a dark diagonal line.

First of all, the positions of the most prominent Fraunhofer lines are located, since they are to a certain extent the scale for the absorption spectra. It is difficult to provide a separate scale in the pocket spectroscope, and for the present purpose it can be dispensed with. The most important Fraunhofer lines are denoted by the initial letters of the alphabet A, a, B, C, D, F, G, h, H' and H". Of the chief lines, A and B occur in the red, C in the orange, D in the yellow, E in the green, F in the blue, G in the indigo, and H in the violet.

The line D in the yellow coincides with the sodium line, and is therefore a convenient guide in locating the other lines. The best plan is to observe the spectrum of ordinary daylight through the main prism whilst the comparison prism is directed towards a sodium flame; by this means it is easy to locate the line lying to the left and the

right of the sodium line, especially with the help of the following table (Fig. 146, p. 1120), in which the positions of the absorption spectra of a few dyestuffs are denoted by curves in the most customary way.

By their height and form the curves represent the intensity of the absorption and its gradual diminution in either direction.

The absorption is greatest at the positions where the curves attain their maximum height.

The table by no means meets present-day requirements and should be regarded only as an explanatory example.<sup>1</sup> J. Formánek<sup>2</sup> has elaborated as the result of numerous observations a spectroscopic method for the estimation of dyestuffs on the following principle.

The form of the absorption spectrum of the solution of the dyestuff and thereby the group, to which the dyestuff under examination belongs, is first determined by means of a spectroscope of suitable dispersion.<sup>3</sup> Formánek distinguishes between the following forms:—

1. A symmetrical band, as for example in Aniline Blue 2B, alcohol-soluble (A.);
2. A band with a faint uniform shading towards the right (Malachite green or Patent Blue [M.]);
3. A band with a faint shading right and left (Bordeaux extra [By.]);
4. A band gradually disappearing to the right (as for example in Sky Blue [C.M.]);
5. A band gradually disappearing to the left (as for example in Benzo Violet R [By.]);
6. A strong band and a weak band on the right (as for example in Rhodamine or Methylene Blue);
7. A strong band and a weak band on the left (as for example in Guinea Violet 4B [A.] or Nile Blue B [B.]);
8. Two weak bands on both sides of a strong band (as for example in Phloxin B [S.] or New Blue R [By.]);
9. Two contiguous equal bands (double bands) (as for example in Chromotrope 2R [M.]);
10. Two unequal undulatory united bands (wavy bands) (as for example in Azo eosin [By.]);
11. One strong band and several weak bands to the right or the left (as for example in Alizarin Green S [M.], Alizarin Garnet R paste [M.] in ethyl alcohol, or Janus Blue G [M.]);
12. A partial absorption (as for example in Naphthol yellow [M.]).

<sup>1</sup> Cf. M. Schütze, *Z. physik. Chem.*, 1892, 9, 109, and especially C. Grebe, *ibid.*, 1892, 10, 673, on "The spectra of azo dyestuffs."

<sup>2</sup> *Z. Unters. Nahr. u. Genussm.*, 1899, 2, 260.

<sup>3</sup> J. Formánek, "Untersuchung und Nachweis organischer Farbstoffe auf spektroskopischem Wege," 2nd ed., Berlin, Julius Springer, 1908; Cf. also *Z. Farb. Ind.*, 1902, 1, 289, 329, 505, 660; 1903, 2, 9, 45, 72, 95, 319, 369.



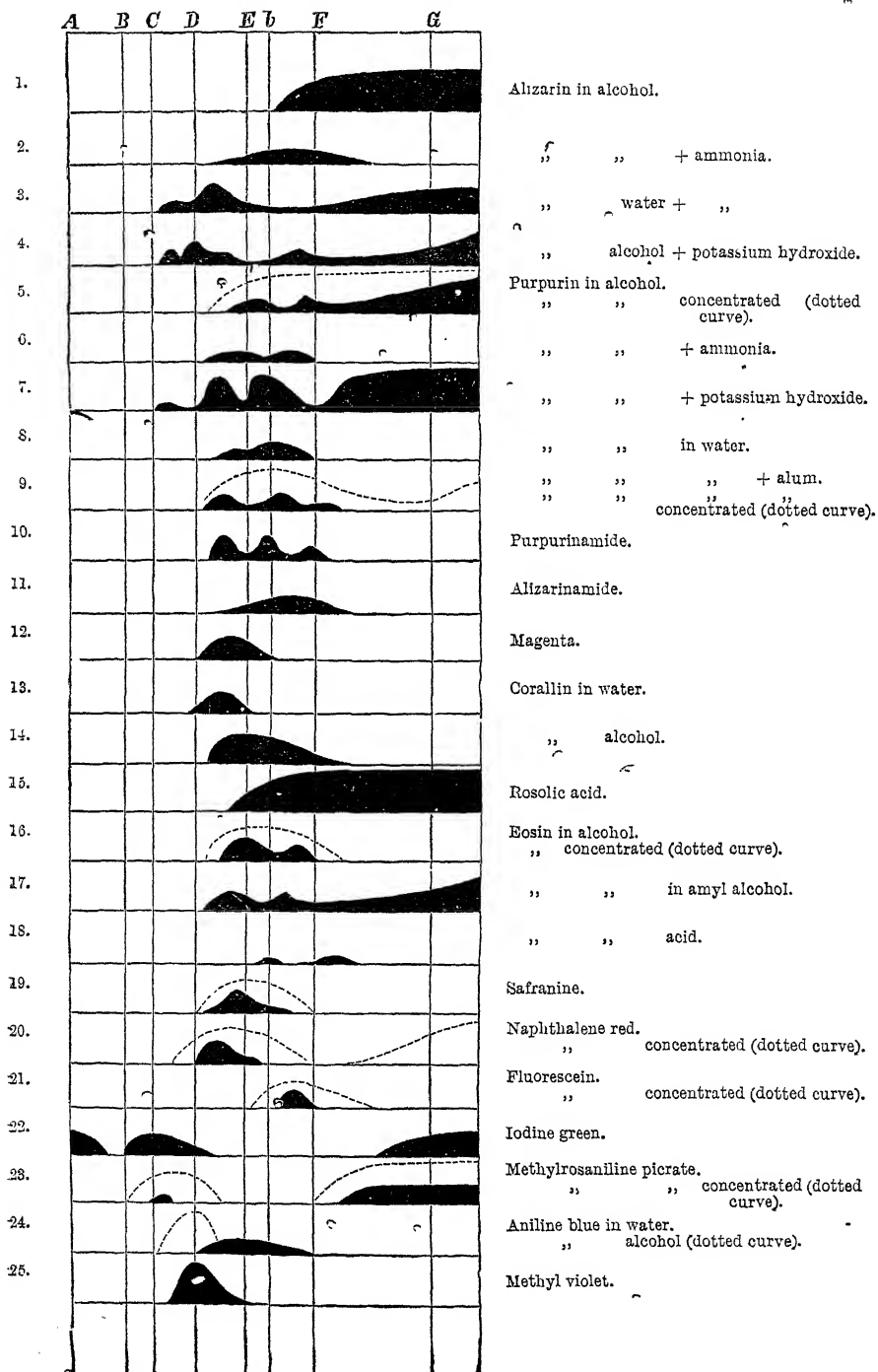


FIG. 146.

Such are the types of absorption bands which are exhibited, as a rule, by the simple dyestuffs.

All dyestuffs are classified in groups and sub-groups according to the form of their absorption bands, thus :

Green dyestuffs in 6 main groups			Red dyestuffs in 6 main groups		
Blue	„	8	„	Yellow	5

By the application of a suitable measuring arrangement to the spectroscope, the position of the absorption band or bands is determined, whereby the dyestuff is even characterised in many cases.

If this is not so, the dilute solution of the dyestuff is divided into three portions; one portion is treated as directed with dilute nitric acid (1 : 5), another with ammonium hydroxide (ammonium hydroxide, sp. gr. 0.96 = 1 : 5), and the third with potassium hydroxide (1 : 10). The change of the colour and in the spectrum is noted.

By means of these observations the dyestuff in question is identified by the help of tables compiled for this purpose, and for details of which reference must be made to Formánek's publications.

A large spectroscope (Zeiss, Krüss, Gustav Meissner) is necessary for absolutely certain analyses; for many technical analyses a pocket spectroscope provided with a scale of wave-lengths (Zeiss) is sufficient.

Formánek uses the following reagents :—

Nitric acid 1 : 5.

Ammonium hydroxide, sp. gr. 0.96 = 1 : 5.

Aqueous potassium hydroxide 1 : 10 (freshly prepared and colourless).

Alcoholic potassium hydroxide 1 : 10 (colourless).

Acetic acid 1 : 5.

Solution of alum 1 : 5.

Solvents : water, 97 per cent. alcohol, amyl alcohol.

Great experience is required to obtain accurate results by this method; even then it is often difficult to avoid making mistakes. It fails utterly in the cases of most yellow dyestuffs and many azo dyes, since either no bands at all or only very indecisive ones are visible, and also the colour reactions of different dyestuffs often appear quite identical or exhibit such slight differences in shade that they are only discernible by a well-trained eye.

Individual dyestuffs, excluding the exceptions mentioned, can as a rule be identified with certainty.

The behaviour of mixtures presents much greater difficulty.

At Gnehm's suggestion forty samples, each consisting of a mixture of two dyestuffs, were examined spectroscopically; successful results were obtained only in isolated cases.

When only small quantities, either in substance or in the form of dyed material, are available for examination, use must be made of this method, the only one which in these circumstances and in ex-

perienced hands can promise success, especially if it is possible to combine it with other reactions.

In such cases the dyestuff for the examination must be extracted unchanged from the pieces of material. This can frequently be effected by 90 per cent. acetic acid or ethyl alcohol, or by amyl alcohol, often also by colourless acetone, and in many cases by the successive use of several solvents. The solutions thus obtained are then submitted to spectroscopic examination.

Lehmann<sup>1</sup> has described a method by which mixtures are first separated by diffusion into jelly, the various parts of which may then be examined spectroscopically.

**Photoscopy.**—By this term P. Heermann<sup>2</sup> denotes the process of systematically testing dyestuffs (in solution or on the fibre) by different sources of light, a process which has been placed on a scientific basis, chiefly by the work of Paterson.<sup>3</sup>

It is based on the fact that many dyestuffs exhibit different shades in light from different sources, and depends on the one hand on the different compositions of lights from different sources, and on the other hand on the different absorption spectra of the dyestuffs. Those colours which show the same shade in daylight exhibit different shades in artificial light if their absorption spectra are different; such a change of shade in artificial light is not observed if the absorption spectra and the other physical properties of the dyestuffs agree. The chemical constitution of the dyestuffs and the method of dyeing on the fibre are of no importance and do not directly affect the photoscopic behaviour. Paterson arranges the different sources of light in groups which exert a similar influence on the shade of the colour.

White diffuse daylight is taken as the normal light, and all changes of the shade are referred to this. Nearest to this come the magnesium light and the electric arc light (first group). Then follows the Welsbach or incandescent gas light (second group), and then in sequence, acetylene light, lime-light, oil lamp-light, ordinary gas light, incandescent electric light, and candle-light (third group).

*Examples of Change of Shade.*—Magenta, safranine, benzopurpurine, and analogous dyestuffs in the artificial lights of group three lose a great part of their bluish tinge since their colour approximates to scarlet red. Wool scarlet and other hydroxyazo-dyestuffs of the same kind become lighter and appear orange. Erythrosin, rhodamine, and the other rose dyestuffs of this group likewise change to orange.

Methyl Orange, Orange G, and the other hydroxyazo orange brands become paler and yellower or even white.

<sup>1</sup> *Z. physik. Chem.*, 1907, 57, 718.

<sup>2</sup> *Koloristische und textilchemische Untersuchungen*, 1903, p. 82. (Springer, Berlin.)

<sup>3</sup> *J. Soc. Dyers and Col.*, 1896, 12, 191; 1902, 18, 90.

Auramine, nitrazine yellow, tartrazine, and all citron yellows become distinctly paler.

Chrysamin and other reddish yellows exhibit less change in artificial light than citron yellows.

Acid green, brilliant green, and other dyes with a yellow tinge retain only a rather stronger yellow tinge.

Malachite green, methyl green, Victoria green, and other bluish greens appear still bluer in gas light.

Cyanine, methylene blue, patent blue, diamine sky blue, and other greenish blues appear greener than in daylight, and retain this tendency also in mixtures.

Alkali blue, night blue, Victoria blue, and other sky blues become darker, acquire a reddish tinge, and occasionally even appear slate grey. A slight addition of citron yellow protects the blue to a certain extent against the disturbing effect of artificial light.

Fast acid blue, azo acid blue, induline, bleu de Lyon, resorcin blue, and other reddish blues become redder.

Composition blues of a blue-green and methyl violet appear redder than a blue of homogeneous composition.

Basic violets, like azo acid violet, etc., suffer loss in their blue tinge and appear so much the redder, the redder the brand. The yellow rays of the artificial light unite with the blue constituents of the violet in producing grey, and therefore heighten the effect of the red constituents of the violet on the eye.

Pale violet becomes rose, dark violet becomes garnet red to bright red.

Archil becomes decidedly redder.

Also a Bordeaux, obtained with alizarin and a chromium mordant on wool, becomes distinctly redder.

Alizarin red on wool with alum mordant becomes paler and yellower, turning to scarlet.

Alizarin-iron-lilac acquires a reddish tinge.

Fustic dyed on wool becomes redder.

Patent-fustin hardly changes at all.

Kamala-orange is also scarcely changed.

Indigo-carmin and other indigo preparations lose their greenish tinge and become redder and dirtier.

Dark indigo blue (vat blue) appears almost blue-black in artificial light.

The method is not suitable for general use: on the one hand, sufficient data, such as are given for example for spectroscopic examination in Formánek's work, are lacking; on the other hand, the expensive apparatus is not at all proportional to the importance of the results hoped for. In special cases, possibly, evidence might be obtained to support the results arrived at by other means in a more satisfactory manner.

II. NATURALLY OCCURRING ORGANIC DYESTUFFS<sup>1</sup>

## I. BLUE DYES

## Indigo.

Indigo is obtained from cultivated or (as in West Africa, etc.) wild-growing indigo plants in East India, Coromandel, Java, China, Central and South America, Brazil, West and North Africa, and many other localities. The most important varieties are *Indigofera tinctoria*, *I. sumatrana*, *I. arrecta*, *I. anil*, *I. disperma*, and *I. argentea*. Accounts of the cultivation of indigo plants and of the production of indigo have been given by Köchlin-Schwartz,<sup>2</sup> Dépierre,<sup>3</sup> and Rawson.<sup>4</sup>

The best kinds of commercial indigo are obtained from Bengal, Java, and Guatemala; in addition to these, indigos from Coromandel, Manilla, Madras, Senegal, Isle of France, Egypt, Caracas, Brazil, Cuba, Jamaica, Domingo, Louisiana, and Mexico are placed on the market.

Many years' experience is required to form an accurate or approximately accurate estimate of the quality of these numerous kinds of indigo from their appearance. The lighter an indigo is, the bluer the colour and the less it is tinged with violet; the more pronounced and the yellower the coppery lustre produced by rubbing, the better is the quality; on the other hand, the higher the specific gravity, the more violet the colour; the darker and the redder the copper lustre of the streak, so much the worse is the quality. When indigo is bought, the colour, the appearance, and the lustre of the fracture should be particularly noted.

The fracture of a good indigo must be uniform and dull, and of a pure blue or violet-blue colour; when rubbed with a smooth substance a pronounced, almost golden, metallic lustre should be produced.

**1. Asiatic Indigo.**—(a) According to v. Cochenhausen, Bengal indigo of all qualities and colours is put on the market.

The following classification and characterisation of the chief kinds of indigo, originating from Girardin,<sup>5</sup> are given unabridged on account of the importance attributed to the testing and examination of indigos in the indigo trade.

The best kinds, which consist of cubical or prismatic pieces, 5 to 8

<sup>1</sup> Cf. v. Cochenhausen, "Natural Dyestuffs still employed in Dyeing," *Z. angew. Chem.*, 1904, 17, 874; Felsen, "Der Indigo und seine Konkurrenten," 1909.

<sup>2</sup> *Bull. Soc. Ind. Mulhouse*, 1857, 28, 307.

<sup>3</sup> *Bull. Soc. Ind. Rouen*, 1876, 434; *Dingl. Polyt. J.*, 1877, 225, 601.

<sup>4</sup> *J. Soc. Dyers and Col.*, 1886, 2, 140; *Chem. Ind.*, 1887, 10, 110; *Zentralblatt für Textil-industrie*, 1890, No. 3.

<sup>5</sup> *Leçons de Chimie élémentaire*, vol. ii., 604.

cm. in length, and contain about 75 per cent. of indigo, have a splendid, dark blue colour, and are finely and uniformly grained; they adhere to the tongue, can be easily powdered, and acquire a coppery lustre by friction with the finger. After these comes reddish violet indigo with a purple shade and a more uniform and glistening fracture; it is denser and harder than the preceding. The red colour depends on the presence of a larger quantity of red and brown substances. Among these are the kinds of indigo which give the best results in the vat. The worst qualities of Bengal indigo, like those from other localities, have a pale blue colour tinged with grey or green. Such a colour indicates the presence of a large amount of foreign substances, which, however, are different from the indigo-brown characteristic of purple indigos, and are quite useless for dyeing purposes. An indigo of this quality is hard and dense, adheres but slightly or not at all to the tongue, and does not acquire a coppery lustre by rubbing.

(b) Coromandel or Oude Indigo resembles the intermediate grades of Bengal indigo, and is put on the market in lumps which are hard, heavy, and only slightly brittle.

(c) Manilla Indigo is obtained from the Philippines, and consists of bright blue lumps which, however, do not give a full coppery streak. The poorer qualities are heavier, and are hard and show a dull blue fracture. Frequently it is contaminated with clay and chalk; it is employed less for dyeing than for blueing.

(d) Madras Indigo has a rough, granular fracture, and gives only a faint coppery streak; it does not contain much dyestuff, is as light as Bengal indigo, and adheres only slightly to the tongue. The cubical pieces still retain the imprint of the support on which the indigo has been dried.

(e) Java Indigo is characterised by the great purity of the dyestuff, since it contains but only small quantities of foreign substances. The small content of dyestuff is due to the presence of clayey constituents.

**2. African Indigo.**—(a) Egyptian indigo consists of large, light, dry, dark blue cubical lumps, which show a pronounced glistening streak and smooth fracture.

(b) Indigo from the Isle of France is brought on the market in small cubes which resemble Manilla indigo.

(c) Senegalese Indigo, which seldom comes into the market, is very much more contaminated with earthy matter than the other kinds. Uncontaminated specimens are very valuable.

**3. American Indigo.**—(a) Guatemala Indigo consists of irregular pieces of different shapes and sizes. It resembles Bengal indigo in its properties; the better qualities are very frequently mixed with inferior grades, so that the estimation is very difficult.

(b) Caracas Indigo is generally equal to Guatemala Indigo, but is less highly valued.

(c) Brazil Indigo is a worse kind, which has usually a deeper blue colour, is hard, rough, and lustreless.

**Constituents.**—It is to be noted that the quality of an indigo and also its content of dyestuff depend less on its source than on the greater or less care exercised during its preparation.

In addition to indigo-blue, indigo contains indigo-brown, indigo-red, indigluten, and mineral matter.

A Bengal indigo of good quality contains approximately

Indigo-blue	61.4
Indigo-red	7.2
Indigo-brown	4.6
Indigluten	1.5
Mineral matter	19.6
Water	5.7
	<u>100.0</u>

The amount of indigo-blue (indigotin) varies (excluding very bad kinds such as occasionally come from West Africa, for example) between 20 and 90 per cent, and averages 40 to 50 per cent. Indigo-red (indirubin) is soluble in alcohol, indigo-brown in alkalis. The latter is present in larger amounts in those kinds of indigo, in the preparation of which lime has been employed. In order to free the indigo-blue as much as possible from the other constituents of the indigo, the indigluten is extracted by dilute acid, the indigo-brown by dilute sodium hydroxide, the indigo-red by boiling alcohol, in this order; the indigo-blue and the insoluble portion of the mineral matter is thus left behind.

An alternative method consists in extracting the indigo-blue and the indigo-red together by Rawson's hydrosulphite-vat process (see below), and subsequently removing the red by boiling alcohol in an extraction-apparatus.

Indigo-blue is more or less soluble in aniline, chloroform, glacial acetic acid (suggested by Lenz),<sup>1</sup> benzene, nitrobenzene, toluene, phenol, creosote, amyl alcohol, acetone, stearic acid, paraffin, and high-boiling petroleum. All of these solutions do not show the same colour. For example, the solutions in chloroform and aniline are indigo-blue whilst that in paraffin (and also in fuming sulphuric acid) has the purplish red colour of indigo vapour, a behaviour which resembles to a certain extent that of iodine.<sup>2</sup> Indigo-blue dissolves in hot concentrated potassium hydroxide with an orange-yellow colour.

The behaviour of indigo towards reducing agents such as hydrosulphurous acid, glucose, zinc dust, stannous oxide, ferrous oxide (vat-

<sup>1</sup> *Z. anal. Chem.*, 1887, 26, 550; 1890, 29, 101.

<sup>2</sup> Nietzki, *Chemie d. organische Farbstoffe*, 5th edition, 1906, p. 333.

formation), and of the resulting indigo-white in the air, is a matter of common knowledge.

Various **Indigo Preparations** (Indigotindisulphonic acid, Indigo-carmin, Indigo-purple, Indigo-violet) are obtained from indigo. Indigotinsulphonic acid is prepared by treating finely powdered indigo with fuming sulphuric acid or with a mixture of the same with ordinary concentrated sulphuric acid until a drop of the liquid forms a clear blue solution in water without leaving an insoluble residue.

When a solution of the indigotinsulphonic acid (sp. gr. 1.162) is largely diluted with water and neutralised by a solution of sodium carbonate or precipitated by saturated brine, sodium indigotindisulphonate,  $C_{16}H_8O_2N_2(SO_3Na)_2$  (Indigo-carmin), is produced, which is insoluble in the sulphate mother liquor but dissolves in pure water. Three brands of indigo-carmin are recognised commercially, which have the following average composition: <sup>1</sup>—

	Water.	Indigo.	Salts.
Carmin I. . . .	89	4.96	5.7
" II. . . .	85	10.02	4.8
" III. . . .	78.7	12.04	13.9

To ascertain the quality of indigo-carmin it is sufficient, according to Mierzinski,<sup>2</sup> to place a small quantity on unsized paper (filter paper). If the product is impure a green ring is quickly formed round the sample. The ring is not produced, however, if the carmin has been well dried; in this case the sample must be first moistened with boiling water in order to obtain a good result. A better method is to dye wool, mordanted with alum and tartar, with a definite amount of the carmin; the whole of the blue dyestuff is thus fixed and separated, whilst the green is not affected and can be subsequently dyed on silk. The undesirable weathering of dried indigo-carmin can be prevented by the addition of 3, to at most, 4 per cent. of glycerol (calculated from the weight of the dry carmin).

When one part of finely powdered indigo in the form of a paste is slowly covered with twenty times its weight of sulphuric acid, the temperature being kept low by external cooling (whereby a larger amount of indigotinmonosulphonic acid is produced), an intensely reddish violet product is obtained after the reaction has proceeded for about half an hour. A drop of the mixture is smeared on a watch-glass and examined against the light; the colour furnishes sufficiently trustworthy evidence of a successful result of the preparation. The mixture is now poured into a large quantity of water, the simultaneously formed indigo-

<sup>1</sup> Girardin, *Leçons de Chimie élémentaire*, vol. ii., 618, 216.

<sup>2</sup> *Die Erd- Mineral- und Lackfarben*, 1881, p. 216.



disulphonic acid is removed by filtration, and the residue, after being washed with water, consists of pure indigo-purple. This can be employed as a satisfactory substitute for Archil, and produces a beautiful violet on unmordanted wool.

Indigo-violet is obtained by a method similar to the preceding, except that the indigo is slightly warmed with the sulphuric acid instead of being kept cool; also a smaller quantity of acid is used.

### Chemico-physical Examination of Indigo.

(a) *Specific Gravity*.—This furnishes some, but by no means conclusive, evidence of the amount of dyestuff in the indigo. In this connection G. Leuchs<sup>1</sup> has compiled the following table:—

Spec. Grav.	Percentage of dyestuff.
1.324	56 to 56.5
1.332	55
1.343	54.5
1.350	53
1.372	49.5 to 52
1.371	49
1.351	47
1.364	46.5
1.381	44
1.384	43
1.412	40
1.432	39
1.437	37
1.455	30.5

The values quoted, it is well to note, are the mean of a series of determinations.

(b) *Moisture*.—An indigo of good quality loses 3 to 7 per cent. of its weight by drying at 100°.

(c) *Ash*.—One gram of the dried indigo is incinerated in a platinum crucible. The percentage of ash in indigo varies very greatly, but the presence of more than 10 per cent. denotes adulteration with mineral matters (chalk, lime, sand, powdered slate, graphite, etc.). These are detected by stirring a portion of the finely powdered indigo in water in a large tumbler, and examining any sediment by the usual methods. Good indigo should float on water and can be distributed throughout the liquid without forming an earthy or sandy deposit.

(d) *Foreign Organic Impurities*.—Powdered indigo should not form a sticky liquid by trituration with a little water (absence of gum or dextrin), and its solution in nitric acid should remain clear after the addition of potassium iodide (the formation of a blue colour denotes the

<sup>1</sup> *J. prakt. Chem.* 1871 [ii.], 4, 349.

presence of starch). Occasionally indigo is adulterated with logwood lake. According to Mierzinski,<sup>1</sup> very frequently powdered indigo of a good quality is placed in the seroons of poorer qualities, whereby the latter acquire a coating of the good product and consequently its external appearance. Instances are on record of the discovery of spurious indigo, consisting of dirt and indigo dust, in the seroons of Guatemala indigo. •

H. Quantin states<sup>2</sup> that in the case of a sample of indigo obtained from Calcutta oxalic acid had been added, the effect of which would be apparently to increase the percentage of indigo, estimated by the permanganate process, in the sample.

*Estimation of Indigo by Dye-Trials.*—The directions given by v. Cochenhausen<sup>3</sup> are as follows:—

One gram of pure indigotin is converted by treatment with 20 to 25 g. of concentrated sulphuric acid into indigotinsulphonic acid, which is dissolved in water, and the solution is diluted to 1 litre. 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20 c.c. of this solution are placed in 20 boiling-vessels, and 500 c.c. of water are added to each. In each of the 20 dye-baths a piece of woollen yarn or fine flannel, which weighs exactly 5 g. and has been carefully defatted in a solution of 10 g. of ammonium carbonate in 1 litre of water at 30° to 40°, and subsequently washed, is dyed while the temperature of the bath is gradually raised to the boiling point. After three-quarters of an hour the pieces are removed from the dye-baths, which are now almost completely decolorised, and, when cold, are washed with pure water, and are dried in the shade. These pieces form a colour-scale which remains unchanged for a long time if it is protected from light and air.

If now 1 g. of a good average sample of the indigo under examination is converted into indigotinsulphonic acid, the product is dissolved in 1 litre of water, and 5 g. of woollen yarn or fine flannel are dyed in 20 c.c. of the solution, it is easy, after a little practice, to find with which standard of the colour-scale the washed and dried piece corresponds in colour. If, for example, the piece corresponds in colour with No. 13 of the scale, 20 c.c. of the solution of the indigo under examination have the same dyeing-value as 13 c.c. of the solution prepared from pure indigotin; the indigo under examination contains, therefore, 65 per cent. of pure indigo-blue.

Such a colour-scale, however, prepared by means of quantities of the dyestuff, which form an arithmetical progression, does not constitute what the dyer terms a "shading." To secure a uniformly graduated scale the amounts of the dyestuff employed in its preparation must form

<sup>1</sup> *Die Erd- Mineral- und Lackfarben*, 1881, p. 200.

<sup>2</sup> *Ann. Chim. Anal.*, 1902, 7, 256.

<sup>3</sup> Muspratt's *Handbuch der technischen Chemie*, 3rd ed., vol. iii., p. 121.

a geometrical progression. A solution of indigotinsulphonic acid, prepared from 0.2 g. of indigotin, is diluted to 1 litre. A piece of woollen yarn, weighing 5 g., is dyed by 100 c.c. of this solution. The resulting colour-standard constitutes the deepest tone of the scale, and has been produced by 20 mg. of the dyestuff. Next, 800 c.c. of the remaining solution of the dyestuff are diluted to 1 litre, and a second 5-g. piece of yarn is dyed by 100 c.c. of the solution; this second colour-standard has been dyed by only  $\frac{8}{10}$  of the quantity of dyestuff employed in producing the darkest standard. Once again, 800 c.c. of the remaining solution are diluted to 1 litre, and a third standard is dyed by 100 c.c. of this solution which contains 12.8 mg. ( $= \frac{8}{10}$  of 16 mg.) of indigo.

If it is desired to ascertain which of the available kinds of indigo is the most economical, cost being taken into account, the dye-trials are performed, not with equal weights of the dyestuffs, but with quantities corresponding with equal prices. Take for an example the four following kinds of indigo:—

	Price per lb.	
	s.	d.
1. Bengal . . . .	5	0
2. Oude . . . .	4	0
3. Kurpah I. . . .	3	0
4. Kurpah II. . . .	2	0

One gram of each is converted into indigotinsulphonic acid by means of concentrated sulphuric acid, and the solution of the product is diluted to 1 litre. If the price corresponds with the amount of indigo-blue, 8 c.c. of the Bengal solution, 10 c.c. of the Oude, 13.3 c.c. of the Kurpah I., and 20 c.c. of the Kurpah II. should produce the same colour. If this is not the case, it is easily ascertained which of the samples is the most economical.

J. Grossmann<sup>1</sup> submits the indigo to a purification by treatment with hot hydrochloric acid and sodium hydroxide, before it is converted into indigo-carminic for the purpose of the dye-trials.

B. W. Gerland<sup>2</sup> converts the indigo by means of sulphuric acid (sp. gr. 1.67) at 100°, first into the insoluble indigomonosulphonic acid, and then changes this into the soluble disulphonic acid by concentrated sulphuric acid at 100°. If the solution of the latter is dark coloured, he recommends a purification of the indigo by hydrochloric acid and hydrogen peroxide before it is employed in the analysis.

<sup>1</sup> *Österr. Wollz.*, 1897, 1076; Fischer, *Jahresber.*, 1897, 630.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1896, 15, 15.

### Colorimetric Examination of Indigo.

According to W. F. Koppeschaar,<sup>1</sup> the methods of extracting indigo have changed in recent years in such a way that former processes of examination are no longer applicable. Modern commercial products contain much more indigo-red (indirubin) (occasionally it exceeds 10 per cent.) than formerly. Consequently it is necessary to estimate the red as well as the indigo-blue. He proposes the following process for this purpose.

1. *Estimation of the Blue in Indigos containing only a small quantity of Red.*—Half a gram of the finely powdered and carefully sieved sample of indigo is digested in a flask, with occasional shaking, with 25 c.c. of pure sulphuric acid for six hours at a temperature not exceeding 60°. The mixture is transferred to a 250 c.c. measuring-flask, and, after being made up to volume, is filtered.

Rejecting the first portion, 25 c.c. of the filtrate are mixed in a beaker with 75 c.c. of saturated sodium chloride, and the precipitated indigo-carmin is filtered, washed with saturated sodium chloride, and dissolved in boiling water in a 500 c.c. measuring-flask, which is subsequently filled to the mark. By means of Laurent's colorimeter the indigo-blue in the solution can be compared very accurately with a solution of pure indigotin containing 0.1 g. per litre.

2. *Estimation of the Blue and the Red in Natural and in Synthetic Indigo.*—The process depends on the facts that indigo-blue is insoluble in acetic acid, whilst indigo-red and indigo-brown are soluble, but are precipitated by diluting or partly neutralising the solution. 0.5 g. of the finely powdered average sample is heated in an Erlenmeyer flask, 8 to 9 cm. in diameter, with 100 c.c. of glacial acetic acid for one hour at 100° on the water-bath, whereby the indigo-red passes into solution. Then the flask is placed in a sloping position such that the liquid is nearly overflowing; when it is cold, the liquid is filtered as soon as all the insoluble matter has settled. The filter-funnel should have a diameter of 8 cm.; the lower part of the neck is stopped with glass-wool, above which pumice stone, in pieces about as small as grains of sand, is placed to within 1 cm. of the conical portion of the funnel. Above this is arranged the actual filtering medium, a layer of ignited asbestos-wool, which is pressed down gently. During the filtration very great care must be taken that none of the undissolved indigo passes into the funnel. The whole of the solution of the indigo-red can be poured off with the exception of about 6 c.c., which can be neglected if the sample contains only a small percentage of the red; if this is not so, a little glacial acetic acid is added to the residue

<sup>1</sup> *Z. anal. Chem.*, 1899, **38**, 1; Cf. also P. T. Hazewinkel, "A New Indigo, its analysis, and that of Indigo pure (B.A.S.F.)," *Chem. Zeit.*, 1900, **24**, 339.

in the flask, and the liquid is decanted from the insoluble matter as completely as possible into the funnel. When the filtration is finished, the glass-wool and the pumice are removed from the neck of the funnel, the asbestos is transferred by a glass rod from the unstopped funnel into the flask, and the funnel is finally rinsed with 50 c.c. of pure sulphuric acid, the rinsings being allowed to run into the flask. By warming the contents of the flask at 70° for two hours, the indigo-blue is converted into the sulphonic acid, the solution of which is poured into a 250 c.c. measuring-flask, and after cooling is made up to volume with water. Twenty-five c.c. of this solution are diluted to 500 c.c.; the amount of indigo-blue in the latter is estimated colorimetrically. The standard solution (0.1 g. of indigotin per litre), used for the comparison, is prepared from pure indigo (*B.A.S.F.*), which is treated with glacial acetic acid at 100°, filtered, and dried.

For the estimation of the indigo-red, the solution is used which has been obtained by the action of the glacial acetic acid on the sample of indigo; 5 to 25 c.c. of the solution in a beaker are partly neutralised by sodium hydroxide (5 c.c. of the glacial acetic acid solution require 12 c.c. of 20 per cent. sodium hydroxide), whereby the red is precipitated. The precipitate is collected, washed with 5 per cent. sodium hydroxide (to remove indigo-brown), dried, placed together with the filter in a 50 c.c. measuring-flask, and shaken with glacial acetic acid; the resulting solution of indigo-red is estimated colorimetrically. The comparison-liquid is a solution containing 0.05 g. of indigo-red per litre. The pure indigo-red is obtained by heating finely powdered Java indigo with glacial acetic acid, filtering off the insoluble blue, and precipitating the red by diluting the filtrate with water. The precipitate is collected and washed with sodium hydroxide to remove the brown. The resulting indigo-red is easily purified by sublimation under diminished pressure.

When an indigo contains more than 10 per cent. of red, the solution of the latter must be diluted with an equal volume of glacial acetic acid. When the percentage of red is very small, the comparison-liquid must be diluted in a corresponding manner.

For the estimation of indigo-red in synthetic indigo, only 0.1 g. is used; otherwise, the process is exactly like the preceding except that the comparison-liquid is prepared with synthetic indigo-red.

W. P. Bloxam and A. G. Perkin<sup>1</sup> have recently devised a method for the quantitative estimation of indigo-red in indigo. The dyestuff, mixed with purified sand, is introduced into a glass tube (25 × 90 mm: approx.) closed at one end with calico, which is placed in a Soxhlet apparatus and the material extracted with pyridine. The pyridine extract is evaporated finally with the addition of hot water, and the precipitate, which consists of indirubin and a little indigotin together

<sup>1</sup> *Proc. Chem. Soc.*, 1910, 26, 168.

with impurities, is collected on asbestos, washed with dilute hydrochloric acid to remove mineral matter, with 1 per cent. alkali to dissolve indigo-brown, and finally with 1 per cent. acetic acid solution. The crystalline residue is dried, sulphonated, and the solution of the mixed sulphonic acids analysed by means of the Duboscq colorimeter.

The residual mixture of sand and crude indigotin is washed in the Soxhlet apparatus with hot 10 per cent. sulphuric acid, which removes indigo-gluten and some mineral matter, and with water until free from acid; the residue is then dried and sulphonated in the ordinary manner, the product dissolved in water, the solution filtered, and titrated with permanganate or titanium trichloride. The accuracy of the process has been determined by an examination of mixtures of pure indigotin and indirubin, and the reliability of the colorimetric work, in respect of the amount of colouring matter present, by means of titanium chloride.

For colorimetric processes, it is necessary, according to Brylinski,<sup>1</sup> to employ a solution of a pure blue colour, that is, one containing exclusively the disulphonic acid. This is prepared as follows:—

A mixture of 1 g. of indigo.  
 „ 20 g. „ powdered glass.  
 „ 20 cc. „ sulphuric acid (sp. gr. 1.84).  
 „ 5 cc. „ fuming sulphuric acid (25 per cent. SO<sub>3</sub>).

is placed in a round-bottomed flask, which is closed and allowed to stand, with frequent shaking, for forty-eight hours at the ordinary temperature.

The indigo can be sulphonated more rapidly (in six hours) by heating to 100°

A mixture of 1 g. of indigo.  
 „ 20 g. „ powdered glass.  
 „ 25 cc. „ sulphuric acid (sp. gr. 1.84).

This method yields solely a sulphonic acid which dissolves in water with a blue colour.

Such a solution is also advantageous in titrimetric methods, because the violet tinge, exhibited by aqueous solutions of the tri- and tetra-sulphonic acids, diminishes the sharpness of the colour change.

### Quantitative Estimation of Indigotin.

**1. Ulzer's Method.**<sup>2</sup>—One gram of the finely powdered indigo is treated with 50 c.c. of aqueous 5 per cent. sodium hydroxide and 10 c.c. of hydrogen peroxide, and the mixture is heated to boiling for ten minutes. After cooling, the mixture is diluted with water to twice its volume, and is filtered through a dry, tared filter

<sup>1</sup> *Bull. Soc. Ind. Mulhouse*, 1897, 67, 332.

<sup>2</sup> *Mitt. techn.-Gew. Museums*, 1892, 214.

paper, 10 to 12 cm. in diameter. If the first portion of the filtrate is turbid, it can usually be clarified by passing it once again through the filter. The precipitate is washed successively with warm water, dilute hydrochloric acid (1:10), water, and boiling alcohol, and is weighed after being dried at 100°. The washing with alcohol is continued until the filtrate is no longer brown or red, but has a light blue colour. The dried indigotin is ignited and the slight amount of residual ash is taken into account in calculating the percentage.

E. Stolba<sup>1</sup> uses a similar process. He extracts with hydrochloric acid, washes with ammonium hydroxide and then with alcohol, weighs, and ignites.

Voeller<sup>2</sup> estimates, by the Kjeldahl method, the nitrogen in the chemically purified indigo, and multiplies the result by 9.36 to ascertain the amount of indigo blue.

In spite of the good results obtained by Tennant<sup>3</sup> and by Lee,<sup>4</sup> methods of estimating indigotin by sublimation cannot be recommended on account of their uncertainty.

The extraction method is based on the treatment of a weighed sample of the indigo with a suitable solvent, and the weighing of the indigotin obtained by crystallisation from the resulting solution.

Hönig<sup>5</sup> extracts the indigo, mixed with powdered pumice, with aniline or nitrobenzene in a special extraction apparatus. The indigotin separates in crystals almost completely from the solution; after diluting the concentrated solution with five to six volumes of alcohol, the indigotin is collected and weighed. In calculating the percentage, a correction must be applied for the solubility of the indigotin in the solvent.

J. Schneider<sup>6</sup> extracts the dyestuff from the sample under examination by boiling naphthalene, which is subsequently separated from the indigotin by ether.

Brandt<sup>7</sup> uses aniline instead of naphthalene in Schneider's process, since naphthalene very easily crystallises out during the filtration of an ethereal solution of naphthalene, and a large quantity of ether is required for washing. In a Soxhlet apparatus, 0.2 g. of indigo is extracted with aniline for a half to one hour. The solution is allowed to cool, whereby the indigotin crystallises out. After the addition of water and hydrochloric acid to dissolve the whole of the aniline, the mixture is filtered through a tared filter; the indigotin is washed with hot water until the filtrate is free from chloride, and finally with

<sup>1</sup> *Färber-Zeit.*, 1894-95, 6, 110.

<sup>2</sup> *Z. angew. Chem.*, 1891, 4, 110.

<sup>3</sup> *J. Amer. Chem. Soc.*, 1884, 6, 185; *Chem. Ind.*, 1884, 7, 297.

<sup>4</sup> *Chem. News*, 1884, 50, 49.

<sup>5</sup> *Z. angew. Chem.*, 1889, 2, 280.

<sup>6</sup> *Z. anal. Chem.*, 1895, 34, 347; Clauser, *Österr. Chem. Zeit.*, 1899, 2, 521.

<sup>7</sup> *Rev. intern. Falsific.*, 1897, 10, 130.

alcohol, which dissolves at the most only 0.5 per cent. of the total quantity of indigotin.

According to A. Brylinski,<sup>1</sup> the estimation of indigotin, by means of boiling aniline, is affected by two sources of error. In the first place, a portion of the indigotin is decomposed (even to the extent of 30 to 40 per cent.) during the prolonged action (three to four hours) of the aniline; secondly, indigotin crystallises from aniline with about 10 per cent. of molecularly combined solvent. Since Brandt only boils the material for half an hour, the two errors approximately counterbalance one another in his process, and the final result is sufficiently accurate.

B. W. Gerland's method<sup>2</sup> depends on the use of the vapour of nitrobenzene.

He has designed a special form of extraction apparatus by which the extraction and crystallisation of the indigotin can be effected in half an hour. The indigotin separates from the cold solution in slender crystals. Only a small fraction thereof remains in the solution, and this source of error is rectified by Gerland by the use of nitrobenzene previously saturated with indigotin in the cold.

The crystals of indigotin still contain 3 to 6 per cent. of impurities, which are removed before weighing by treatment with hydrochloric acid or, better, with hydrochloric acid and hydrogen peroxide.

Gerland states that the estimation is affected by an error of 0.1 to 0.2 per cent., because indirubin is somewhat more easily soluble than indigotin in cold nitrobenzene.

According to Rawson,<sup>3</sup> indirubin is not only somewhat, but is very much more easily soluble than indigotin in cold nitrobenzene; consequently he considers that the error is greater than the above.

A. Brylinski<sup>4</sup> proposes glacial acetic acid as a solvent. The principle of the method depends on the fact that glacial acetic acid, at the boiling point, can dissolve considerable quantities of indigotin, which is insoluble, however, in 20 to 30 per cent. acetic acid at the ordinary temperature. The operation is performed in a Soxhlet apparatus, and suffers, of course, from the disadvantage of requiring a fairly long time. Cohabitation for five hours is necessary for the exhaustive extraction of 0.150 g. of indigo. When the extraction is complete, the glacial acetic acid solution is poured into a beaker and diluted with four times its weight of cold water. The precipitate is collected on a tared filter, washed with boiling water, with alcohol, and with ether, dried at 110°, and weighed.

A new process for the quantitative estimation of indigo in substance

<sup>1</sup> *Bull. Soc. Ind. Mulhouse*, 1898, 68, 33.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1896, 15, 15.

<sup>3</sup> *J. Soc. Dyers and Col.*, 1896, 12, 83.

<sup>4</sup> *Bull. Soc. Ind. Mulhouse*, 1898, 68, 37; *Rev. Gen. Mat. Col.*, 1898, 2, 52.



and on the fibre described by R. Möhlau and M. R. Zimmermann<sup>1</sup> is as follows:—

The indigo is powdered and passed through a silk-sieve, No. 10-16; 0.1 g. is then weighed into a glass bottle of 100 c.c. capacity containing a few Bohemian garnets, and is covered with 50 c.c. of a mixture of 100 c.c. of glacial acetic acid and 4 c.c. of concentrated sulphuric acid; the whole is warmed for fifteen minutes on a vigorously boiling water bath, and is occasionally rotated. The solution is filtered through a toughened paper-filter, 10 c.c. in diameter, moistened with acetic-sulphuric acid or through a Neubauer platinum crucible into a 300 c.c. beaker. The bottle and the filter are rinsed and washed with warm acetic-sulphuric acid until the washings are colourless; this requires another 50 c.c. Yet a third 50 c.c. of the acetic-sulphuric acid mixture is added to the filtrate, which is then heated to 70° and treated with 100 c.c. of boiling hot water while it is being vigorously stirred with a glass rod. At first the water is added drop by drop, but as soon as the indigo blue begins to separate in crystals it is added in a thin stream. The mixture is allowed to cool spontaneously, and is then filtered through a weighed Neubauer platinum crucible or through a tared toughened filter-paper dried at 105°. The residue on the filter is washed first with 50 c.c. of hot dilute hydrochloric acid (1:10), then with 50 c.c. of hot water, and finally with 2 or 5 c.c. of cold 95 per cent. alcohol. The crucible on the filter-paper is dried at 105° for an hour and then weighed.

The indigo-blue thus obtained still contains about 0.2 per cent. of ash which can be estimated after ignition. The ash must be taken into account when dealing with natural indigos, but can be neglected in the case of the synthetic product, because only one-third of its weight enters into the calculation (see below).

In this form the method is exact for the estimation of indigo-blue in natural indigo.

When dealing with the analysis of *Synthetic Indigo* it must be borne in mind that it may contain 3 to 10 per cent. of red dyestuff, of which only 75 per cent. remains in the solution when the blue is precipitated. The true percentage of the indigo-blue is only ascertained, therefore, when the analytical operations are continually repeated on the precipitated indigo-blue until the filtrate is no longer red but colourless.

The percentage of indigo-blue is accurately and more simply determined by calculation. To the percentage of indigo-blue determined by the preceding process is added the sum of the percentages of the moisture, ash, and organic foreign matter. The difference between the total and 100 corresponds with 75 per cent. of the

<sup>1</sup> *Z. Farb. Ind.*, 1903, 2, 189.

red dyestuff. The true percentage of indigo-blue is obtained, therefore, by subtracting one-third of this difference from the percentage of indigo-blue determined analytically.

The percentage of moisture is calculated from the loss of weight of 0.5 g. of indigo after two hours' drying at 105°.

The percentage of ash is calculated from the loss of weight, after ignition in a platinum crucible, of 0.5 g. of the indigo dried at 105°.

The weight of insoluble organic foreign matter is conveniently ascertained in a Neubauer platinum crucible. The residue remaining in the crucible has only to be washed thoroughly with hot water, and the crucible to be dried at 105° for one hour and weighed. This organic residue includes the ash; its correct percentage is obtained, therefore, only after ignition, etc. Grandmougin<sup>1</sup> maintains that this method is unsuitable in practice.

Of the numerous processes involving reduction and oxidation, only a few will be mentioned which are either quite trustworthy or rapidly performed. A very complete collection and critical examination of the various processes for the estimation of indigo has been given by v. Cochenhausen.<sup>2</sup> Also Rawson<sup>3</sup> has very thoroughly investigated the various methods of estimating indigo.

**2. Reduction (Vat) Processes.**—As a rule such processes give a too low percentage of dyestuff, consequent on the reduction of a portion of the indigo-white to compounds which do not regenerate indigo-blue on oxidation. All vat methods where alcohol (in which indirubin is soluble) is employed (as for example, Rau's modification of Fritsche's process<sup>4</sup>), share with Hönig's extraction method the disadvantage that the indigo-blue alone is estimated. However, reduction methods are very well adapted—if the blue and the red are estimated together, or the latter, if desired, can be subsequently determined by extracting the weighed precipitate with alcohol in an extraction apparatus—for the examination of indigo which is also to be employed as a vat. Oxidation methods are preferable, on the other hand, when the indigo under examination is to be used for the preparation of indigo-carmin, etc.

A rapid estimation is possible by Owen's method.<sup>5</sup> One gram of the finely powdered indigo is weighed on a watch-glass, dried at 100°, made into a very thin paste by trituration with water, and washed into a 250 c.c. measuring-flask. After the addition of 3 g. of zinc dust and 6 g. of sodium hydroxide the flask is filled slightly above the mark,

<sup>1</sup> *Z. Farb. Ind.*, 1903, 2, 275.

<sup>2</sup> *Leipziger Monatschrift f. Text-Ind.*, 1888, 3, 406, 456, 506; cf. also the same author's summary of the processes of estimating indigo in Muspratt's *Handbuch der technischen Chemie*, 1889, vol. iii., pp. 153-162.

<sup>3</sup> *Chem. News*, 1885, 51, 255; 1888, 57, 7, 19, 29, 34.

<sup>4</sup> *J. Amer. Chem. Soc.*, 1885, 7, 16.

<sup>5</sup> *Ibid.*, 1889, 11, 178.

since the volume diminishes somewhat after one to two hours. The flask is shaken occasionally. The formation of reddish or brownish streaks in the yellow liquid is a sign that the reduction is proceeding too far (and therefore that the result will be decidedly too low). Frothing occurs if too much zinc is present. When the reduction is complete 50 c.c. of the clear liquid are withdrawn and allowed to oxidise in the air for a quarter of an hour. The liquid is then acidified with hydrochloric acid, and passed through a filter (dried at 100° or counterpoised against another filter); the precipitate is washed carefully, dried at 100°, and weighed. The more recent modification of Rawson's process<sup>1</sup> is used when indigo is to be estimated as accurately as possible by a vat method. For this purpose a solution of hyposulphite is required. Zinc turnings are placed in a bottle of about 100 c.c. capacity, and covered with a solution of sodium hydrogen sulphite, sp. gr. 1.30. The bottle is corked and kept for about one hour, at the end of which the odour of sulphur dioxide is not perceptible. The liquid is decanted into a bottle and thoroughly mixed with 1 litre of water in which about 10 g. of recently burnt lime are suspended. The clear liquid is withdrawn and kept beneath a layer of petroleum. One gram of the powdered indigo is then made into a thin paste with water and placed in a glass flask into which 500 to 600 c.c. of lime-water are introduced. The flask is closed by a four-holed rubber stopper. Two of the holes serve respectively for the entrance and exit of coal gas; through the third passes a siphon provided with a pinch-cock, whilst the tube of a separating-funnel is fitted into the fourth. After the air in the flask has been displaced by coal gas, the liquid is heated to about 80° and 100 to 150 c.c. of the sodium hyposulphite solution are run in from the separating-funnel; the mixture is kept nearly at the boiling point for half an hour, after which the solid matter is allowed to settle, 500 c.c. of the clear liquid are withdrawn, and the volume of the residual liquid is determined accurately.

The 500 c.c. of liquid are placed in an Erlenmeyer flask and air is drawn through for twenty minutes, whereby the excess of hyposulphite is oxidised to sulphite and the indigo-white to indigo-blue. After the addition of hydrochloric acid to dissolve any calcium carbonate which may have been formed, the precipitate of indigotin and indirubin is collected on a tared filter (weighed after drying at 100°, or counterpoised against a second filter), carefully washed, dried, and weighed. Too high results are obtained when ferric salts are present in the indigo solution reduced by the hyposulphite. The method gives very good results but requires special care.

A similar method is recommended by M. Allhausse.<sup>2</sup>

<sup>1</sup> *Chem. News*, 1888, 57, 7, 19, 29, 34.

<sup>2</sup> *Z. angew. Chem.*, 1898, 11, 288.

Brylinski<sup>1</sup> proposes first to sulphonate the indigo under examination and then to titrate the solution of indigo-carmin with a standard hyposulphite solution. The details of his method are as follows. Commercial sodium hydrogen sulphite is diluted until its specific gravity is 1.25; 100 c.c. of the solution are shaken for five minutes with 20 g. of zinc dust in a flask, diluted to 1 litre, neutralised by lime, and filtered quickly. For actual use the solution is diluted five times.

The apparatus (Fig. 147) consists of a bottle with three tubulures. Through the first passes a separating funnel, through the second a glass tube which is connected to the burette by rubber tubing provided with a pinch-cock; the third tubulure is fitted with a two-holed rubber stopper through which pass the tube by which gas enters and circulates in the bottle and the tube for the exit of the gas which is burnt in any suitable burner.

A definite quantity of the indigo-carmin is placed in the apparatus and is reduced by the addition, drop by drop, of the necessary amount of hyposulphite solution. Then a measured quantity of the standard indigo solution is run into the bottle from the separating funnel and the amount of hyposulphite is determined, which is required for its reduction. For example, if

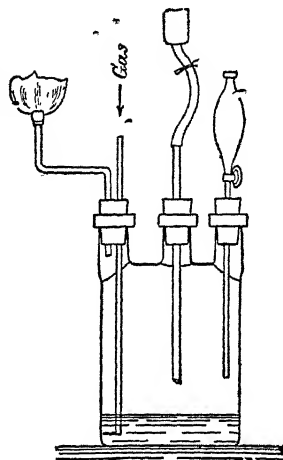


FIG. 147.

25 c.c. of indigo pure<sup>2</sup> require 10.1 cc. of hyposulphite,  
and 25 c.c. of commercial indigo<sup>2</sup> require 4.7 c.c. of hyposulphite,

then the commercial product contains 47 per cent. of the standard indigo (type).

This method has two disadvantages, namely, working in a current of gas, and the great instability of the hyposulphite solution, which very rapidly alters its titre in the air.

G. Engel<sup>3</sup> has also elaborated a volumetric process. The indigo is converted into indigo-carmin, which is then titrated with standard vanadyl sulphate.

A solution of vanadyl sulphate absorbs atmospheric oxygen, and also rapidly changes its titre by keeping in an incompletely filled, even though stoppered, bottle. The titre changes considerably even whilst the solution is being poured from the bottle into the burette. In order to avoid these difficulties the estimation is performed in a current of carbon dioxide.

<sup>1</sup> *Bull. Soc. Ind. Mulhouse*, 1897, 67, 336.

<sup>2</sup> Two grams of the indigo per litre in the form of sulphonic acid.

<sup>3</sup> *Bull. Soc. Ind. Mulhouse*, 1897, 67, 337.

*Preparation of the Vanadium Solution.*—Ten grams of ammonium vanadate are dissolved in 100 g. of sulphuric acid of sp. gr. 1.84 by gentle warming, the red liquid is poured into 2 litres of water at 50°, 50 g. of zinc dust are added, and the mixture shaken until a persistent bluish violet colour is produced. The solution is then filtered and allowed to cool.

A measured volume of the indigo solution is placed in an Erlenmeyer flask provided with a side tube. The flask is closed by a two-holed cork; through one hole passes a narrow glass tube, which is connected to the burette by rubber tubing provided with a pinch-cock; into the other hole is fitted a bent glass tube, by which the entering carbon dioxide is led to the bottom of the flask. A Dupré burette is used (see Fig. 148). Although it appears complicated, the apparatus is excellently adapted for such titrations. The burette is also filled with carbon dioxide, and as long as the current is continued the titre of the vanadium solution remains the same.

*Details of the Titration.*—

First of all, a type solution is prepared with the purest obtainable indigo, and is titrated with potassium permanganate. As is well known, this method yields good results in the case of pure indigo. The solution of vanadyl sulphate is standardised with this indigo solution. As a precautionary measure the carbon dioxide, before entering the

apparatus, is passed through wash-bottles containing vanadyl sulphate, which absorbs any oxygen present. It is also advisable that all water used in the estimation should be boiled and allowed to cool in a current of carbon dioxide.

With these precautions very good results are obtained. The error caused by the possible presence of compounds of iron in the indigo solution (the presence of which is easily detected by ammonium hydroxide) is eliminated as follows. Vanadyl sulphate is rapidly oxidised in the air to vanadous sulphate (green solution), which reduces ferric salts but not indigo. If a small excess of this green solution is added to a solution of indigosulphonic acid containing a little ferric

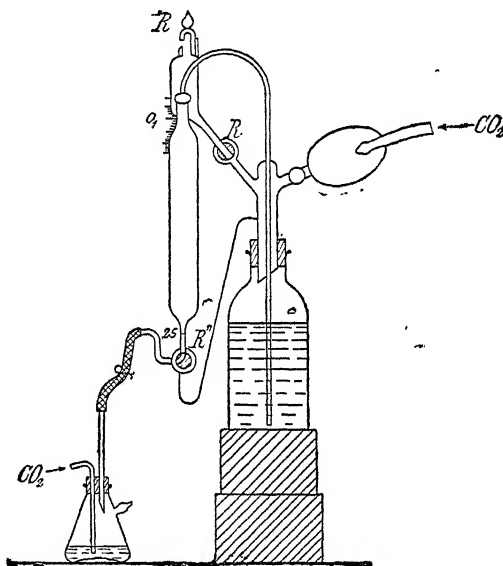


FIG. 148.

chloride, the same result is obtained in an actual titration as with an equal quantity of the indigo solution free from iron. Care must always be taken not to add too great an excess of the green solution, which has a prejudicial effect on the sensitiveness of the reaction.

The following expedient can also be adopted:—A weighed quantity of the indigo is treated with nitric acid and is calcined, and the iron in the ash is estimated. Again the action of the vanadyl sulphate solution on the ferric salt is ascertained by titration. The disturbing influence of the iron in the reaction can be calculated from these data. A. Wangerin and D. Vorländer<sup>1</sup> employ hyposulphite for the titration of indigo as follows:—

*Preparation of the pure Indigo.*—The brand “Indigo pure B.A.S.F. in powder,” containing 98 per cent. of indigo, is refined by reduction. For this purpose one part of indigo is dissolved in

12	parts of sodium hydroxide, sp. gr. 1.21,
30	„ concentrated hyposulphite,
10	„ water,

by digesting the mixture at 40° to 50° in an atmosphere of coal gas with occasional gentle shaking. When the indigo has dissolved the vat is filtered as rapidly as possible, and the indigo is precipitated with air from the clear yellow or greenish filtrate.

The indigo is collected, according to its amount, on a toughened filter paper or on fine linen, and is washed successively with hot water, hot dilute hydrochloric acid (1 litre of water, 30 c.c. of pure, fuming hydrochloric acid), water (until free from hydrochloric acid), and finally, repeatedly with alcohol and a little ether. The indigo is then dried at 105° to 110° until its weight is constant. In this way 16 to 18 g. of pure indigo are obtained from 20 g. of the commercial product. It is assumed to be 100 per cent. indigo, and is used as the standard in the determination of the indigo solutions under investigation.

*Sulphonation of the Indigo.*—One gram of the 100 per cent. indigo, powdered as finely as possible, is covered in a small, dry flask with 10 c.c. of 94 per cent. sulphuric acid, and the mixture is heated with occasional shaking, for a half to one hour in a boiling water bath. After cooling, the liquid is poured into a beaker containing 100 to 180 c.c. of water; the blue solution is passed through a toughened filter-paper (the object of filtering is to ensure that no particles of indigo have escaped sulphonation), which is then well washed with warm water; when quite cold, the solution is diluted to 1 litre.

*Preparation of the Hyposulphite Solution.*—Half a litre of bisulphite solution, sp. gr. 1.37 to 1.39, is saturated with sulphur dioxide, and diluted with 750 c.c. of water. Into the solution, cooled externally by

<sup>1</sup> *Z. Farb. Ind.*, 1902, 1, 281. Cf. also the pamphlet on Indigo of the B.A.S.F., 1900, 26; Binz and Kupperath, *Färber-Zeit.*, 1903, 14, 225.

ice, is introduced slowly a paste of 35 g. of zinc dust and 250 c.c. of water, the mixture being gently rotated and a current of coal gas being passed through the apparatus during the addition. After being kept for one to two hours, the clear solution is drawn off into a 2-litre flask containing 200 c.c. of 25 per cent. milk of lime, and the mixture, after being thoroughly shaken once, is allowed to remain overnight in an atmosphere of coal gas. The clear liquid is then decanted from the deposit and is treated with a few c.c. of potassium hydroxide (5 to 7.5 c.c. of a solution, sp. gr. 1.383) until the solution is distinctly alkaline.

The approximate strength of the hyposulphite solution is next determined by allowing it to fall, drop by drop, from a graduated siphon into 50 c.c. of 0.1 per cent. indigo solution in a small flask until the latter is decolorised; 50 c.c. of 0.1 per cent. indigo solution require 1.5 to 2 c.c. of hyposulphite prepared under the preceding conditions.

As a rule, it is advisable to use a hyposulphite solution, of which 30 to 40 c.c. are required for the titration of 100 c.c. of 0.1 per cent. indigo solution (factor, 0.02 to 0.03).

The hyposulphite solution retains its titre during the morning or the afternoon, provided it is covered with a layer of benzene, is kept in an atmosphere of coal gas, and is made alkaline, as directed above.

Trustworthy and concordant results are obtained in the titration *only when the ratio of indigo to water remains the same*. For every addition of water a corresponding correction, proportional to the quantity of atmospheric oxygen introduced with the water, must be applied. To ascertain the correction accurately, 50 c.c. of 0.1 per cent. indigo solution are titrated alone, and also in the presence of various measured quantities of distilled water.

Example :

	I.	II.	III.	IV.	V.	VI.	VII.
50 c.c. of the indigo-solution.	c.c. of Hypo-sulphite solution.		Difference between I. and II.	Difference calculated for 50 c.c. of water.	Average correction for the water added.	Corrected values (difference between IV. and V.).	Difference between I. and VI.
Undiluted . . . . .	16.20	...	...	...	...	...	...
Diluted with 50 c.c. of water .	...	17.3	1.10	1.10	1.10	16.20	0.00
" 100 " . . . . .	...	18.38	2.18	1.09	2.20	16.18	- 0.02
" 150 " . . . . .	...	19.60	3.40	1.13	3.30	16.30	+ 0.10
" 200 " . . . . .	...	20.50	4.30	1.07	4.40	16.10	- 0.10
" 250 " . . . . .	...	21.75	5.55	1.11	5.50	16.25	+ 0.05

In this case the correction for the atmospheric oxygen in water

amounts to 2.20 c.c. of the hyposulphite solution for every 100 c.c. of water.

Moreover, in calculating the factor of the hyposulphite solution a correction must be applied for the atmospheric oxygen in the water in which the indigo has been dissolved. Account need not be taken of the sulphuric acid used in dissolving the indigo. The correction, therefore, is the value determined as above for distilled water.

The factor of the hyposulphite solution is calculated as follows:— One thousand c.c. of  $N/1$ -hyposulphite represent 1 g.-equivalent of indigo, *i.e.*, 131 g. Therefore, 1 g. of indigo is equivalent to 7.633 c.c. of  $N/1$ -hyposulphite.

Suppose 50 c.c. of 0.1 per cent. standard indigo solution (= 0.05 g. of indigo) require 16.20 c.c. of the prepared hyposulphite solution; the corrected value, after subtracting 1.10 c.c. for the 50 c.c. of water in the indigo solution, is  $16.20 - 1.10 = 15.10$  c.c.

The factor of the prepared hyposulphite solution is then calculated from the equation

$$15.10 : 0.05 \times 7.633 = 1 : f$$

$$f = 0.02527.$$

The correction for the atmospheric oxygen in each 100 c.c. of 0.1 per cent. indigo solution is termed the water-value; in the present example it amounts to  $2.20 \times 0.02527 = 0.0556$  c.c.  $N/1$ -hyposulphite.

The numbers obtained for the water-value agree upon the whole, but always vary so much with the temperature of the water and the time it has been kept that they cannot be regarded as constants corresponding with the solubility of air in water. The water-value must be specially determined for each series of analyses. Wangerin and Vorländer give the following table of values obtained at the ordinary temperature, 17—20°:—

Employed in the titration.	$N/1$ -Hyposulphite used.	$N/1$ -Hyposulphite theoretically required.	Water-value = correction expressed in c.c. of $N/1$ solution.	Correction per cent.
0.1 g. of indigo in 100 c.c. of aqueous solution.	0.8178	0.7633	0.0545	6.7
	0.8212		0.0579	7.1
	0.8236		0.0603	7.3
	0.8189		0.0556	6.8
	0.8237		0.0604	7.3
	0.8234		0.0601	7.3
	0.8246		0.0613	7.4
	0.8172		0.0589	6.8
	0.8176		0.0543	6.6
	0.8122		0.0489	6.0
	0.8122		0.0489	6.0
	0.8122		0.0489	6.0

*Analyses by means of the modified Hyposulphite Process.*—After preparing the standard solution of 100 per cent. indigo and also the



solution of the indigo under examination, with ordinary distilled water, measured volumes of both solutions are titrated with hyposulphite. The water-value is determined by titrating a known volume of the standard indigo solution which has been diluted with a known volume of distilled water. The water must be kept under the same conditions as the indigo solutions.

For example, the following numbers have been obtained in the analyses of Bengal indigo :—

One gram of 100 per cent. indigo in 1000 c.c.

	Hyposulphite.
100 c.c. require	31.60 c.c.
100 c.c. + 100 c.c. of water	33.94 c.c.

One gram of Bengal indigo per 1000 c.c.

	Hyposulphite.
100 c.c. require	21.80 c.c.

Therefore, the water-value for 100 c.c. of indigo solution is  $33.94 - 31.60 = 2.34$  c.c. This has to be subtracted from the hyposulphite used ; therefore

	Hyposulphite.
100 c.c. of 0.1 per cent. standard indigo solution require	29.26 c.c.
100 c.c. „ 0.1 „ Bengal „ „	19.46 c.c.

The equation

$$29.26 : 0.1 = 19.46 : x$$

gives  $x = 0.0665$

The Bengal indigo contains, therefore, 66.5 per cent. of indigo.

Knecht<sup>1</sup> employs titanous chloride as reducing agent. One gram of the sample is sulphonated with 5 c.c. of concentrated sulphuric acid, the solution diluted to about 300 c.c. and poured into a 500 c.c. graduated flask. Twelve grams of chalk are then added to the warmed solution, and after evolution of carbon dioxide has ceased, the contents are made up to 500 c.c. When the precipitate has settled (twenty to thirty minutes), 50 c.c. of the clear solution are withdrawn and transferred, along with 25 c.c. of a 20 per cent. Rochelle salt solution, to a conical flask, provided with an india-rubber stopper having three holes, one for the introduction of carbon dioxide, a second for the escape of the gas, and the third for the tube attached to the burette containing the titanous chloride (1 c.c.  $\text{TiCl}_3 = 0.001557$  g.  $\text{Fe} : 112 \text{ Fe} = 262$  indigotin). The titanous chloride is run in until the blue colour changes to yellow. In making the calculation an allowance must be made for the calcium sulphate and calcium carbonate. In the following examples this was determined experimentally, and the

<sup>1</sup> *J. Soc. Dyers and Col.*, 1905, 21, 292.

actual amount of indigo solution was found to be 499 c.c. instead of 500 c.c. :—

Indigo.	Percentage found.		
	By $\text{TiCl}_3$ .	By $\text{KMnO}_4$ (Rawson).	Gravimetrically (Mühlau and Zimmerman).
Bengal I. . .	59.08	59.14	58.5
II. . .	55.97	56.00	57.0
Kurpah . . .	35.32	...	30.0
Fig. . . .	32.61	32.47	33.5

Both indigotin and indirubin are reduced by titanous chloride, so that with artificial indigos which may contain indirubin, the results are too low.<sup>1</sup>

**3. Oxidation Processes.**—Mohr's original permanganate process<sup>2</sup> has been materially improved by Rawson,<sup>3</sup> who seeks to remove as completely as possible, by precipitating and washing the indigotin-sulphonic acid by a solution of sodium chloride, the impurities in the indigo, which also reduce the permanganate, and consequently exert a prejudicial effect by causing the results to come out too high.

One-half to one and a quarter of the finely powdered indigo is first mixed with an equal weight of powdered glass. The mixture is then introduced gradually and with constant stirring into 20 c.c. of concentrated sulphuric acid, sp. gr. 1.845, the mortar being rinsed with a little powdered glass. After heating for one hour at 90–95°, the resulting indigotinsulphonic acid is diluted to 1 litre and filtered, and 50 c.c. of the filtrate are mixed with 50 c.c. of water and 32 g. of sodium chloride in a small Erlenmeyer flask. The mixture is filtered after two hours, and the precipitate, after being thoroughly washed with a saturated solution of sodium chloride, is dissolved in hot water, 1 c.c. of sulphuric acid is added, and the solution is diluted to 300 c.c. and titrated with a solution of potassium permanganate containing 0.5 g. of the salt per litre. At first no change is appreciable in the deep blue colour, but slowly it alters through green to pale yellow. This (not the formation of a red colour) constitutes the end-point, which is sharp and easily detected. A correction has still to be applied for the slight solubility of sodium indigotinsulphonate in saturated sodium chloride solution, which amounts to 0.0008 g., according to Rawson. It is essential that the titration should always be performed under as nearly as possible the same conditions, and, in particular, with nearly the same quantities of actual dyestuff. Rawson states that this oxidation method gives the same results as his reduction process described above.

<sup>1</sup> For a discussion on this process, cf. Bloxam, *J. Soc. Chem. Ind.*, 1906, 25, 735; Bergtheil and Briggs, *ibid.*, 729; Knecht, *J. Soc. Dyers and Col.*, 1906, 22, 330.

<sup>2</sup> *Dingl. polyt. J.*, 1854, 132, 363.

<sup>3</sup> *Chem. News*, 1885, 51, 255.

According to Rawson,<sup>1</sup> samples of Java indigo give permanganate values by the preceding method which are higher than those corresponding with their dyeing strengths. This is due to a yellow dyestuff, the presence of which is best detected by covering a small portion of the powdered indigo in a basin with sodium hydroxide or ammonium hydroxide, whereby a deeply coloured solution is produced.

In estimating the indigotin in such cases, a weighed portion is heated with dilute ammonium hydroxide or, better, with alcohol, and is filtered through asbestos; the residue on the filter is then dissolved in sulphuric acid, as in the usual process for the estimation of indigo. (Barium chloride is found to be a better precipitating agent than sodium chloride, as described in the process of 1885.) It should be noted that the indirubin as well as the yellow dyestuff is dissolved by the alcohol of the ammonium hydroxide.

Grossmann<sup>2</sup> recommends the following modification of Rawson's process. One gram of indigo is heated for an hour at 90° with 20 g. of sulphuric acid (sp. gr. 1.845), and the product is diluted to 1 litre with water; 100 c.c. of the solution are carefully neutralised by pure, weighed calcium carbonate. The impurities are precipitated along with the calcium sulphate whilst indigotindisulphonic acid remains entirely in solution. The precipitate is allowed to settle, and one-half of the solution is filtered and titrated with potassium permanganate which has been previously standardised by pure indigo.

Bergtheil and Briggs<sup>3</sup> prefer to precipitate the impurities with barium sulphate as follows:—

Half a gram of finely powdered indigo is placed in a small narrow-necked stoppered bottle, and mixed with a few Bohemian garnets; 20 c.c. of pure concentrated sulphuric acid are added, and the bottle, with its stopper removed, placed in a shallow water-bath containing just enough water to cover the depth of acid in the bottle. The bath is now brought to the boil, and when briskly boiling, the stopper is replaced in the bottle, which is shaken periodically for fifteen minutes. At the end of this time the bottle is removed from the water-bath, and allowed to remain in cold water with its stopper removed until the contents are cool. These are then transferred to a 500 c.c. flask in which 10 c.c. of a 20 per cent. barium chloride solution and sufficient sulphuric acid to precipitate all the barium has previously been placed, and the whole made up to volume, well shaken, and set aside for the precipitate to settle for one hour. An aliquot part of the supernatant liquid is then titrated with approximately *N*/50-permanganate, and the result calculated on the basis that 1 c.c. of *N*/50-permanganate is equivalent to 0.0015 g. indigotin.

<sup>1</sup> *J. Soc. Chem. Ind.*, 1899, 18, 251.

<sup>2</sup> *Ibid.*, 1906, 25, 729.

<sup>3</sup> *Ibid.*, 1905, 24, 308.

E. Donath and R. Strasser<sup>1</sup> submit the indigo, before sulphonation, to a special process of purification for the following reasons.

The valuation of an indigo does not coincide with its content of indigotin, because in actual indigo-dyeing the intensity of the colour, the shade, is probably affected by the presence of indigo-red and indigo-brown. Nevertheless, the dyeing strength, *i.e.* the efficiency of the indigo as a dyestuff, is determined in the greatest degree by the amount of indigo-blue. The determination of this amount, therefore, is of prime importance in ascertaining the quality of the indigo.

One gram of the very finely powdered indigo is weighed into a glass-stoppered weighing bottle, and is mixed therein very intimately with four times its bulk of thoroughly ignited pumice granules, about 1 mm. in diameter, by shaking and turning the bottle. At the bottom of a Soxhlet-Szombathy extraction apparatus a compact layer of asbestos is so arranged that it effectively closes the opening of the siphon tube without projecting too far up the tube of the extraction apparatus, otherwise a stoppage may very easily occur during the later stages of the extraction. The layer of asbestos must extend a little above the highest point of the siphon tube. Above the asbestos is placed a thin layer of ground pumice, then the mixture of indigo and pumice, and above this the sand with which the weighing bottle has been rinsed. The whole contents of the extraction tube are about 5 cm. deep. The extraction tube is now connected below with a boiling-flask containing distilled water, and above with a Liebig's condenser, the end of the inner tube of which is widened somewhat into a funnel shape to facilitate the addition of liquids. The water in the flask is then boiled vigorously; if the water condenses in the extraction tube and collects above a certain height, a little dilute hydrochloric acid is poured in through the tube of the condenser. After, at most, fifteen minutes' boiling, or after the repeated addition of dilute hydrochloric acid, the glutinous matter is completely extracted and the degelatinised mass is thoroughly washed, by allowing hot water to flow into the extraction tube. The flask, which contains a hydrochloric acid solution of the glutinous material, is removed, and the extraction tube is connected to a flask half-filled with a mixture of four parts of alcohol and one part of ether. By placing the flask in a boiling-water bath, the indigo-red is extracted completely, the end of the extraction being recognised by the fact that the liquid siphoning from the extraction tube, originally intensely brownish red, becomes colourless or has at most a scarcely appreciable bluish colour. The apparatus is then disconnected and the extraction tube is placed in an ordinary drying oven, and freed completely from alcohol and ether at 100–110°. Then the projecting end of the siphon tube is plugged

<sup>1</sup> *Z. angew. Chem.*, 1894, 7, 11, 47.

with asbestos, and sufficient concentrated sulphuric acid, about 30 c.c., is placed in the extraction tube to just cover its contents, and the apparatus is suspended by copper wire in an air-bath. This air-bath (Fig. 149) consists of a copper cylinder (A), closed at the bottom, which

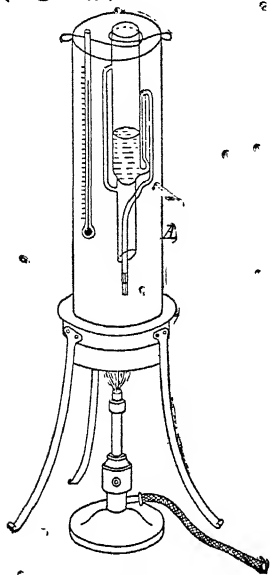


Fig. 149.

is supported vertically on a tripod by means of a ring soldered on it, and can be heated from below by a gas flame. A thermometer is suspended in the air-bath. After the apparatus has been maintained at 80° for one and a half or, at most, two hours, it is safe to assume that the sulphonation of the indigotin is complete. The apparatus is withdrawn from the bath and allowed to cool, the asbestos plug is removed from the lower end of the siphon tube, the apparatus is held over a litre flask and distilled water is poured in at the top, whereby the solution of indigotinsulphonic acid is removed and flows into the flask; if the contents of the apparatus, especially the asbestos, cannot be completely freed from indigotinsulphonic acid by cold water, the contents are transferred into a porcelain basin and the last trace of the indigotinsulphonic acid is removed by boiling with water. The combined liquids in the litre flask are allowed to cool and the flask is then filled to the mark with distilled water. Two estimations are performed with the thoroughly mixed blue solution; 100 c.c. are diluted with 400 c.c. of water and titrated with potassium permanganate (of such a concentration that 1 c.c. represents 0.0099139 g. of indigotin) until the green colour has disappeared completely.

The permanganate solution is best standardised by pure indigotin; in order to work under as nearly as possible the same conditions, 1 g. of pure indigotin is taken, and the quantity of sulphuric acid and amounts of water used for dilution are the same as in the preceding estimation. The whole experiment requires about three hours.

According to W. Holtschmidt,<sup>1</sup> the permanganate process is affected by two sources of error.

1. Sulphur dioxide is evolved during the sulphonation if the heating is too strong.
2. The difficulty of detecting the end-point in the subsequent titration of the indigotinsulphonic acid solution with potassium permanganate.

The first error is obviated by preventing any noticeable development of heat during the sulphonation and also during the subsequent dilution with water. It is advisable not to sulphonate by warming with

<sup>1</sup> *Z. angew. Chem.*, 1899, 12, 451, 475.

concentrated sulphuric acid, but to employ concentrated sulphuric acid containing 40 per cent. of phosphoric oxide, whereby the sulphonation is effected in a shorter time at the ordinary temperature. The process is as follows:—

One-half or one gram of the finely powdered, undried indigo is weighed into a test tube about 7 cm. long and about 2 cm. in diameter, and is covered with 10 c.c. of the concentrated sulphuric acid containing 40 per cent. of phosphoric oxide; the mixture is well stirred with a glass rod, placed in a desiccator, and again stirred from time to time. The sulphonation is complete after about two hours; but in order to ensure that the whole of the indigo has been converted into the disulphonic acid, the test tube may be kept overnight in the desiccator. The sulphonated mass is then poured through a funnel into a 500 c.c. or 1 litre flask, and after rinsing the test tube with cold water, the solution is diluted nearly to the mark and is made up exactly to volume when it is quite cold. The solution is rapidly filtered through a large double filter paper, and 25 c.c. of the filtrate are diluted with 100 to 125 c.c. of water in a large porcelain basin and titrated with  $N/100$ -potassium permanganate.

(The solutions should be titrated soon after they are prepared, since they become weaker by several units per cent. by keeping, for example, in a few weeks.)

The best way to avoid the second source of error is to titrate, not by the colour, but by the turbidity, because otherwise with certain kinds of indigo an accurate determination of the end-point cannot be obtained with certainty. The permanganate solution is added drop by drop (about 120 to 130 drops per minute) until the liquid has only a faint green colour, whilst a dark turbidity appears when the liquid is stirred after the addition of the last drop of permanganate. The permanganate is now added, two or, still better, four drops at a time, the liquid being stirred gently once so that the turbidity is not disturbed, and attention is directed to the latter. When this has disappeared completely, the amount of permanganate used is read off and 0.1 or 0.2 c.c. (according as the permanganate has been added two or four drops at a time) is subtracted from the amount. If the permanganate is added too quickly, a considerable excess may be introduced. Moreover, the amount of water used is by no means immaterial; if too much is present, the last appearance of the turbidity may easily be overlooked, particularly in an unfavourable light.

#### 4. Bloxam's Tetrasulphonate Method.<sup>1</sup>—Preparation of Pure

<sup>1</sup> W. P. Bloxam, *J. Chem. Soc.*, 1905, 87, 974; *J. Soc. Chem. Ind.*, 1906, 25, 735; I. Q. Orchardson, S. H. Wood, and W. P. Bloxam, *ibid.*, 1907, 26, 4; R. Gaunt, F. Thomas, and W. P. Bloxam, *ibid.*, 1174; Bloxam, "Report to the Government of India on Research work on Indigo," 1908; cf. also Bergtheil and Briggs, *J. Soc. Chem. Ind.*, 1907, 26, 182; Rawson, *J. Soc. Dyers and Col.*, 1906, 22, 306.

*Indigotin.*—This is necessary in order to serve as a standard. Dry and finely powdered crude indigo is placed in a long-necked Jena flask connected with a water-pump, a catch-bottle being inserted between the flask and the pump. The pressure is reduced as far as possible, and the flask is lowered into a bath of fusible metal previously heated to  $420^{\circ}$ . A square of asbestos cardboard is so arranged that the portion of the flask between the level of the fusible metal and the asbestos cardboard is raised to such a temperature that only indigotin vapour is there present, and that this zone of the flask remains quite clean at the close of the operation, the sublimate being deposited in the upper portion of the flask above the asbestos card. In this way a yield of 60 per cent. can be obtained.

*Method of Analysis.*—The indigotin is dried at  $110^{\circ}$ , and after cooling in a desiccator, 1 g. is weighed out into a small (1 oz.) spouted beaker. To the indigotin is added 2 to 3 g. of purified sand, and 5 c.c. of fuming sulphuric acid (20 per cent.  $\text{SO}_3$ ) is run in from a burette. After well stirring with a short glass rod, the beaker is covered with a watch-glass and heated in the water-oven for twenty minutes (crude indigos are sulphonated with 25 per cent. fuming acid for thirty-five minutes), stirring being repeated at intervals. After cooling, the sulphonic acid is poured into a 500 c.c. flask containing some water, and finally the beaker, stirring rod, and sand are repeatedly washed with water; when cold, the solution is made up to the mark with water (when 500 c.c. = 1 g. of indigotin + 5 c.c. fuming sulphuric acid).

The following solutions are necessary:—

(a) *The precipitant*, a filtered solution of potassium acetate, 450 g. per litre.

(b) *The isotonic*, prepared by adding 5 c.c. of glacial acetic acid to 200 c.c. of the precipitant, and then to 4 c.c. with water.

The analysis is carried out as follows:—One hundred c.c. of the indigotin solution (of 1/500 concentration) is delivered by a pipette into a fairly capacious conical spouted beaker. To this is now added from a burette (provided with a constant supply of the precipitant solution) 80 c.c. of the precipitant. Precipitation is observed when the solutions are well agitated in the conical beaker. The beaker and its contents are now well warmed until complete solution is attained. Cooling is now effected in a stream of running water, and when the contents of the flask are water-cold, the beaker is transferred to a vessel containing ice and water. Here the beaker is left for one hour, during which time the tetrasulphonate settles out as a fine-grained crystalline precipitate, which will filter well. Meanwhile the isotonic solution is placed in a spouted conical beaker and cooled by immersion in ice and water. The whole is filtered by suction through a Gooch crucible, the paper in which is set by a small quantity

of the cooled isotonic solution. With good manipulation the operation is complete in a few minutes. In the case of pure indigotin a carefully performed analysis will yield a filtrate almost colourless. The very pale blue colour can be imitated by diluting a solution of tetrasulphonate of known indigotin value. In this way the indigotin strength of the filtrate, when the process is working well, is estimated at one part of indigotin in three millions of water, a loss which is entirely negligible. The Gooch crucible is now placed in a funnel which rests in the neck of a 200 c.c. flask. With the aid of hot water this is washed free from blue, and any precipitate which adheres to the walls of the conical beaker is dissolved and added to the main fluid, which on cooling is made up to the mark. Portions of this solution are used for the estimation of indigotin:—

(a) *By means of Potassium Permanganate.*—Twenty c.c. of the solution are transferred to a shallow porcelain dish and 80 c.c. of distilled water and 0.5 c.c. of pure concentrated sulphuric acid are added. This solution, which is not of a greater concentration than 1 in 5000, is titrated with the solution of potassium permanganate (1 in 1000), until the addition of a drop produces no longer a cloud in the pure yellow liquid. Indigotin (100 per cent.) would require in these circumstances 9.0 c.c. of permanganate, and percentages are calculated from this standard.

(b) *By means of Titanium Trichloride.*—In this case 25 c.c. of the solution of potassium tetrasulphonate is used for each estimation. This volume of solution is delivered into a conical Erlenmeyer flask of Jena glass of 300 c.c. capacity; to it is added 1.5 c.c. of a 20 per cent. solution of normal sodium tartrate, and the liquid is raised to boiling point, and then titrated while hot with a current of carbon dioxide passing through the flask.

For the estimation of indican in the leaf, Bloxam treats the aqueous extract with isatin, and weighs the indirubin formed. Five grams of dry leaf are placed in a dry glass filter funnel provided with a paper, the base of which is fitted with an india-rubber tube and clip. The clip is closed and the leaf is rapidly covered with boiling water and allowed to remain so immersed for about a minute; the clip is then removed, and when the liquid has filtered through, the leaf is washed several times with water at 60°.

To test whether extraction is complete, the last washings are collected separately and treated with a little 4 per cent. sulphuric acid and 2 per cent. ammonium persulphate, and warmed to 60°, when there should be no production of blue if the extraction has been rightly carried out. As some specimens of leaf show a considerably higher content than 0.94 per cent. indigotin (on which proportion the process was established), a correspondingly larger volume of water is required



for complete extraction. It is advisable in such cases to make the extract up to 1 litre, and to withdraw portions for each estimation. The most suitable volume for estimation is 250 c.c., and the solution is best of such a strength that this volume yields approximately 0.1 g. of indirubin; for this purpose 0.1 g. of isatin and 15 to 20 c.c. of pure hydrochloric acid are required. Air is expelled from the flask by means of a current of carbon dioxide, which is maintained during the whole time of the experiment. The mixture of isatin and plant extract is boiled for five to ten minutes, and the acid is then run in slowly by means of a stoppered funnel (time of flow, five to seven minutes); the liquid meanwhile is boiled very gently, whilst the gas current is increased to guard against entrance of air to the flask. The mixture is boiled for twenty to thirty minutes, cooled in a current of cold water, and the precipitate collected on a tared paper, washed very thoroughly with 1 per cent. sodium hydroxide solution at 70°, and then with 4 per cent. acetic acid, and dried in the water-oven till of constant weight.

**5. Bergtheil and Briggs's Method.**<sup>1</sup>—For the estimation of indigotin in indigo-yielding plants, Bergtheil and Briggs use the following modification of Rawson's<sup>2</sup> method. Twenty grams of leaf are extracted with boiling water, the extract cooled to 45—50°, and 5 c.c. of strong hydrochloric acid and 2 c.c. of a 5 per cent. solution of ammonium persulphate added. The solution is then allowed to remain for at least an hour, and a small portion then removed and filtered through the asbestos filter ultimately to be used for the filtration of the indigotin precipitated. The filtrate is a clear yellow colour, but if the colour becomes green on standing, the filtrate is returned to the main volume and no further persulphate is added until a test portion shows the action of the first addition of 2 c.c. complete; if the yellow colour of the filtrate is permanent, a few drops of persulphate solution are added to it, and if a green colour is then produced, the filtrate is returned to the main solution, together with another 2 c.c. of persulphate solution. When a test portion no longer turns green either on standing or by further addition of persulphate, the reaction is complete, and the solution may then be boiled and filtered, and the indigotin estimated as previously described.

**Criticisms of the Methods for the Estimation of Indigotin.**—In recent years the various processes for the examination of indigo have given rise to an animated controversy. The following are the more noteworthy opinions expressed:

According to Möhlau,<sup>3</sup> in the analysis of natural indigo the hyposulphite and the acetic-sulphuric acid methods give approximately the

<sup>1</sup> *J. Soc. Chem. Ind.*, 1906, 25, 729; 1907, 26, 1172.

<sup>2</sup> "Report on the Cultivation and Manufacture of Indigo," 1904.

<sup>3</sup> *Z. angew. Chem.*, 1903, 16, 547.

same results, the vat-method yields results which are too low, whilst, the permanganate process and the hyposulphite method, in which the water-value is not taken into account, give too high results.

Even when the water-value is taken into account, the accuracy of the hyposulphite method is only apparent and fortuitous, because the other organic constituents of the indigo oxidise hyposulphite. In the case of synthetic indigo, the acetic-sulphuric acid method gives considerably lower values than the hyposulphite and the permanganate methods, because it alone directly estimates the indigo-blue; the vat process yields too low results, because in such methods 4 to 10 per cent. of the pure indigo-blue is decomposed.

Möhlau (1905) is of opinion that the acetic-sulphuric acid process is the best and most convenient.

Binz<sup>1</sup> suggests the estimation of indigos employed in dyeing and printing by the hyposulphite (with exclusion of air) or the permanganate process; the former for natural, the latter for synthetic, indigo. For the preparation of indigo and indigo-carmin, Binz maintains that it is necessary to employ the known oxidation and reduction processes both volumetrically and gravimetrically.

W. Zänker<sup>2</sup> makes the following statement:—

“ . . . Among analysts it has been shown that the usual modern methods of estimating indigo give discordant results, and experts affirm that at the present time we still do not possess an entirely satisfactory process for the determination of the dyeing-value of an indigo. It must always be admitted that a good analysis is a better means for the evaluation of an indigo than dye-trials by vat-methods on a small scale. Quite apart from the fact that, in general, accurate values are never obtained by dye-trials, the vat-method in the laboratory is naturally always quite untrustworthy, and the final result depends more on sundry trivial contingencies than on the quality of the indigo. In actual work the value of an indigo is best and most certainly ascertained by a control of the amount employed and the amount sent out; this, of course, involves the supposition of an accurate and convenient vat-method, and it is only in this way that the accidents occurring in the vat-process can be properly accounted for. This test should be carried out over as long a period as possible.

“ When it is necessary to decide between the values of two kinds of indigo within the course of a few hours, accurately weighed amounts of the dyestuffs, corresponding with the prices, are dissolved in fuming sulphuric acid in the cold or in concentrated acid (sp. gr. 1.84) on the water-bath. The amounts of indigo should weigh between 2 and 3 g.; the sulphuric acid solution is washed into a litre flask and is made up to

<sup>1</sup> *Z. angew. Chem.*, 1903, 16, 572.

<sup>2</sup> *Färber-Zeit.*, 1903, 14, 369; cf. also Brylinski, *Bull. Soc. Ind. Mulhouse*, 1897, 67, 331.

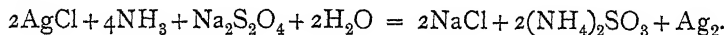
volume. Equal quantities of these solutions are then used to dye equally heavy woollen skeins in pale shades; these colours then determine not only the greater or smaller economy of one or other of the indigos, but also their purity. Although this test is obviously only provisional and approximate, it is easily and rapidly performed, and possesses the great advantage that the results agree, as a rule, with those of the vat-process."

Mention may here be made of Schlumberger's chlorine test,<sup>1</sup> which yields only approximate results but yet is frequently employed. Equal weights of the samples of indigo to be compared are separately dissolved in ten to twelve times the quantity of fuming sulphuric acid, and each solution is diluted with the same quantity of water. The blue liquids are placed in glass cylinders and treated with a freshly prepared solution of bleaching-powder of known strength until the blue colour of the indigo has disappeared. The resulting values are compared with those obtained with pure indigotin prepared by the sublimation of indigo.

**6. Other Tests connected with the Use and Examination of Indigo.**—Reference may be made to the following tests, which are of practical value as regards indigo.

1. *Estimation of Hyposulphite.*—The hyposulphite solution, which is employed in indigo-dyeing for the preparation of the hyposulphite vat, is estimated by Dawson<sup>2</sup> by means of an indigotinsulphonic acid, which is obtained by dissolving one part of purified indigo in ten parts of the best fuming sulphuric acid, warming at 50–60° for about two hours (until a sample of the mixture dissolves completely in water), and diluting to 100 c.c. with water, so that the solution contains 1 per cent. of indigo. This solution keeps without altering. Five c.c. of it (0.05 g. of indigo) are diluted with, and are rendered alkaline with ammonium hydroxide; the hyposulphite solution is run in from a burette until the change of colour shows that the whole of the indigo is reduced. The amounts of indigo and of hyposulphite suitable for work on the large scale are then easily calculated.<sup>3</sup>

Seyewetz and Bloch<sup>4</sup> add excess of an ammoniacal solution of silver chloride to the hyposulphite solution and weigh the metallic silver which is precipitated. The reduction proceeds according to the equation:



Knecht and Hibbert's method<sup>5</sup> for the analysis of solid sodium hyposulphite consists in adding a weighed quantity (about 0.2 g.) to

<sup>1</sup> *Dingl. polyt. J.*, 1842, 84, 369.

<sup>2</sup> *J. Soc. Dyers and Col.*, 1889, 5, 93; *Z. anal. Chem.*, 1890, 29, 629.

<sup>3</sup> Cf. also A. R. Frank, *Z. Elektrochem.*, 1904, 10, 451; A. Binz and H. Bertram, *Z. angew. Chem.*, 1905, 18, 168.

<sup>4</sup> *Rev. Gen. Mat. Col.*, 1906, 10, 101.

<sup>5</sup> *Ber.*, 1907, 40, 3819.

25 c.c. of a solution of methylene blue containing 10 g. of the dyestuff per litre. The methylene blue solution is contained in a conical flask through which a slow current of carbon dioxide is maintained. On dissolving in the methylene blue solution, the hyposulphite reduces its equivalent of the dyestuff, and the excess is estimated, after adding acetic acid, by titration with standard titanium trichloride. The presence of bisulphites or sulphites in the hyposulphite does not interfere with the accuracy of the estimation.

2. *Estimation of Indigo on the Fibre.*—Renard's method<sup>1</sup> of estimating indigo on the fibre is also of practical value. A reducing solution is first made by mixing 100 c.c. of sodium hyposulphite, prepared from sodium bisulphite of 35° Bé., with 100 c.c. of milk of lime, and diluting the mixture to 2 litres. Ten grams of the materials are then warmed with this solution to 60–70°, whereby the indigo is rapidly reduced and the material and the liquid become yellow. Coal gas is then passed through the flask containing the liquid, which is occasionally shaken, and finally the colourless solution is rapidly decanted, still in a current of coal gas, into a measuring cylinder, the volume of the cold liquid (about 100 c.c.) is measured, and the liquid is treated with hydrochloric acid, and filtered after twenty-four hours; the precipitate is collected on a small filter, thoroughly washed, and dried. The precipitate, together with the filter, is then treated with about 10 c.c. of fuming sulphuric acid, and the indigo dyestuff is titrated by Müller's process.<sup>2</sup>

In this way Renard finds 1.1 to 3.6 per cent. of indigo dyestuff (calculated on the weight of the material) in samples of cotton dyed with indigo.

In the same way can be calculated the amount of indigo in materials which have been bottomed with aniline grey, or have been dyed with aniline blue or aniline violet.

Brylinski<sup>3</sup> proposes the use of the glacial acetic acid process for determining the amount of indigo on the fibre. With some modifications the process, according to the researches of A. Binz and F. Rung,<sup>4</sup> is free from objections, and is the best of all hitherto proposed methods.

According to the directions of Binz and Rung, the following are suitable quantities for 10 g. of cotton; 150 c.c. of glacial acetic acid, poured after the extraction into 300 c.c. of water. By heating over a naked flame the operation is completed in three to four hours. Brylinski proceeds now to filter at the pump. A better plan is to add 150 c.c. of ether, in which the whole of the indigotin remains

<sup>1</sup> *Bull. Soc. Chim.*, 1887, [ii.], 47, 41; cf. also A. Binz and F. Rung, *Z. angew. Chem.*, 1898, II, 904.

<sup>2</sup> *Jahresber. f. Chem.*, 1874, 1019.

<sup>3</sup> *Rev. Gen. Mat. Col.*, 1898, 2, 52; 1899, 3, 5; *Bull. Soc. Ind. Mulhouse*, 1898, 68, 287.

<sup>4</sup> *Z. angew. Chem.*, 1898, II, 904.

suspended. The lower layer of dilute acetic acid is removed in a separating funnel, and need not be filtered. The ethereal suspension filters very rapidly, and the precipitate is subsequently washed with alcohol and ether, and is finally treated as described on p. 1135.

Möhlau and Zimmermann<sup>1</sup> estimate indigo on the fibre as follows. About 10 g. of the dyed material, cut into exceedingly small pieces, are placed in a flask or beaker of 250 c.c. capacity, and are covered with 50 c.c. (for cotton), or 200 c.c. (for stout woollen cloth) of acetic-sulphuric acid (a mixture of 100 c.c. of glacial acetic acid and 4 c.c. of concentrated sulphuric acid); the mixture is heated, with occasional shaking, for half an hour on a vigorously boiling-water bath. The hot blue solution is decanted from the macerated fabric through a porcelain funnel fitted with a perforated disc covered with a toughened paper moistened with acetic-sulphuric acid, and the residue, if incompletely extracted, is again heated for twenty minutes with 50 c.c. of acetic-sulphuric acid, the solution is again decanted, the macerated material is transferred to the filter, and the flask and the residue are washed with warm acetic-sulphuric acid until the washings are colourless. About a further 50 c.c. are necessary for this purpose, consequently the volume of the filtrate amounts to about 150 to 300 c.c.

The filtrate is warmed to about 50°, and one and a half to two volumes of boiling water are slowly stirred in. The solution is allowed to cool spontaneously, whereby the indigo-blue separates completely in fine crystals, which are collected on a tared, toughened filter-paper, and are washed first with hot water until free from sulphuric acid, then with 1 c.c. of 95 per cent. alcohol, and finally with 100 c.c. of ether. The filter and the indigo-blue are dried at 105° until the weight is constant, and are then weighed.

In the case of vat-dyed cotton, 0.22 must be subtracted from the percentage of indigo-blue; this amount represents the quantity of modified cellulose which is dissolved by the acetic-sulphuric acid and thus becomes mixed with the indigo-blue.

When vat-dyed wool is heated in the same way, the keratin which is formed is completely soluble in water, and therefore need not be taken into account.

This process can be performed more rapidly than Brylinski's, and gives the most accurate results. After numerous experiments A. Binz and F. Rung<sup>2</sup> arrive at the following conclusions:—

1. The accuracy of the acetic acid process should not, as heretofore, be tested by experiments in which commercial synthetic indigo is extracted with glacial acetic acid.

2. "Indigo pure" and chemically pure indigo are partially decom-

<sup>1</sup> R. Möhlau, M. R. Zimmermann, and J. L. Fitzke, *Z. Farb. Ind.*, 1903, 2, 192.

<sup>2</sup> *Z. angew. Chem.*, 1902, 15, 557.

posed when they are boiled with glacial acetic acid in the presence of a woollen material. Consequently, the results obtained by extracting vat-dyed wool with glacial acetic acid and subsequently titrating the indigo, are too low.

3. On the average the resulting error is 0.1 per cent. of the weight of the fibre. The acetic acid process, therefore, is always available as a comparative method. The acetic acid process gives satisfactory comparative results in the case of cotton.

Knecht's process<sup>1</sup> consists in dissolving the dyed cotton fabric in warm sulphuric acid, diluting with water to precipitate the indigo, and finally sulphonating the dyestuff and titrating in the usual manner. Four grams of the sample of dyed cloth are cut up into small pieces and placed in a porcelain beaker; 25 c.c. of 80 per cent. sulphuric acid (148° Tw.) are now added, and the whole is stirred slowly, the temperature being maintained at about 40°. In a very short time the cloth begins to dissolve, and after about ten minutes' stirring all has passed into solution. The contents of the beaker are now diluted to about 120 c.c. with water, boiled for a few minutes, and the precipitated indigotin is filtered off through a Gooch crucible containing, as filtering medium, first a layer of coarsely crushed quartz of about the size of millet seeds, then a layer of fine quartz of about the size of grain sugar, and lastly a layer of finely divided silica. The depth of the whole filter bed will be about  $\frac{1}{8}$  inch. The filtration is gradually assisted by means of the vacuum pump, which is turned full on towards the end of the operation. The crucible is then dried at 110–120°, and is then placed in a weighing bottle with a small amount of concentrated sulphuric acid, when it is heated for an hour in a water-oven. The sulphonated indigotin is then taken up with water and titrated either by means of titanium trichloride, or by Rawson's permanganate process.

If the amount of indigo contained in the dyed material is small, the whole of the diluted sulphuric acid solution of the indigo is rendered alkaline in a fairly large conical flask by adding soda crystals (55 g. for each 10 c.c. of sulphuric acid used in sulphonating), and is then rendered acid again with tartaric acid before titrating.

A groundwork of logwood or sanders wood on cloth dyed with indigo is detected, according to Philipps, by warming the fabric with dilute nitric acid (1 : 6). A straw-yellow colour is produced if the material has been dyed with pure indigo, whilst a more or less brownish colour is developed when a groundwork has been employed.

F. H. van Leent<sup>2</sup> recommends the following process for the detection of indigo on wool. The fabric, unravelled into loose fibres, is covered with pure molten phenol in a test tube, and is heated and frequently

<sup>1</sup> *J. Soc. Dyers*, 1909, 25, 135, 160.

<sup>2</sup> *Z. anal. Chem.*, 1900, 39, 92; *Chem. Zeit.*, 1900, 24, 121.

shaken for one hour in a boiling-water bath, whereby the indigo is completely dissolved after a repetition of the process. The blue solution is poured off, and the fibres are twice or thrice washed with alcohol and squeezed. The residual wool is pure white when only pure indigo was originally present. By treating the blue solution with a large quantity of alcohol the indigo-blue is mostly precipitated, whilst the solution exhibits a red colour due to the indigo-red which is simultaneously extracted by the phenol.

Of other blue dyestuffs, indophenol alone is removed from the fibre by phenol.<sup>1</sup> When a fabric which has been dyed with various dyestuffs—for example, indigo, anthracene blue, indigo, and sanders wood—is examined by the preceding method, only the indigo is dissolved, and the fibres, examined under the microscope, are partly colourless and partly blue and reddish brown.

### Logwood.

Logwood (Campechy wood) is obtained from the tree *Hæmatoxylon Campechianum*, which flourishes in Central America and in the Antilles, and consists of the stems freed from the bark and the white sap (alburnum). The extract of the logwood is prepared as a viscous liquid (sp. gr. 1.16—1.26), and also in the solid form. The hæmatoxylin present in the logwood produces a grey-violet colour with alumina mordants, evidently due to the aluminium lake of hæmatein produced by atmospheric oxidation.

Copper salts produce a dark blue, and ferric salts and also potassium dichromate a deep black colour. Dyeing and printing with logwood are rather complicated processes, in which several of these mordants are frequently employed simultaneously. For example, to produce a black colour the dyestuff is fixed by an aluminium mordant and the printed material is passed slowly through a solution of potassium bichromate or copper sulphate. Evidently the production of a black colour depends on the formation of higher oxidation products of hæmatein, which have still not yet been studied from a chemical point of view.

Cloths dyed with logwood, unlike those dyed with indigo, do not become white by rubbing and prolonged use.

Logwood varies in quality according to its origin. Campechy wood from the Bay of Campechy is the best; average qualities come from Domingo, Honduras, and Jamaica, the poorest qualities from Martinique and Guadeloupe. Brühl<sup>2</sup> states that Jamaica roots are decidedly the worst source of logwood.

Good logwood should yield about 15 per cent. of dried extract;

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Chem. Zeit.*, 1900, 24, 767.

Brühl<sup>1</sup> remarks, however, that the yields of extracts of logwoods are generally quoted too high. The ground logwood, which is also placed as such on the market, is occasionally moistened with water to prevent loss of the dust, whereby it acquires a bright red colour, which subsequently becomes paler. Sprinkling with lime-water, which is also done to improve the colour, depreciates the dyeing value.<sup>2</sup> Hæmatein, not hæmatoxylin, is to be regarded as the substance which produces the coloured lakes. The process of oxidation, which is necessary for the formation of the hæmatein, occurs, partly before the rasped wood is employed in the preparation of a dye-bath or in the production of liquid and solid extracts, partly during the process of dyeing (by potassium bichromate in the case of wool, by a ferric salt for cotton and silk). Before being extracted, however, the rasped wood is moistened with about one-third its weight of water, and is submitted for two months to so-called "fermentation" (a process of fermentative oxidation), being frequently stirred over during this period; this operation and the accompanying action of the ammonia in the air (sometimes the wood is moistened with dilute ammonium hydroxide or with stale urine) induce the formation of hæmatein. In spite of the introduction of artificial dyestuffs, logwood and its liquid and solid extracts are, even at the present day, of very great importance in dyeing, although not so much so in calico printing. It yields the cheapest and finest bluish black dyestuffs for wool (Chrome Black and Iron Black); it is also still used a little in cotton dyeing.

**Extracts of Logwood and of Dye-woods in general.**—The quantities of extract,<sup>3</sup> prepared from logwood and employed in dyeing (and to a less extent in calico printing), are considerable, and are increasing annually. Von Höhnelt<sup>4</sup> describes the microscopic examination of logwood and of other dye-woods (in the ground state).

According to Schreiner (*loc. cit.*), the reaction of a logwood extract can be ascertained by the colour of the solution. Neutral solutions are deep red, alkaline solutions are blue-red, unfermented (see above), acid solutions are light yellow, and fermented acid solutions are orange-yellow. Extracts to which tannin has been added always have an acid reaction, and the colour, unlike that of the naturally acid extracts prepared under pressure, is not instantly changed to the red of the neutral solution by dilution with water containing a little lime, or by shaking and warming with a small quantity of calcium carbonate. Moreover, the reactions with stannous chloride are characteristic,

<sup>1</sup> *Loc. cit.*

<sup>2</sup> v. Cochenhausen, Muspratt's *Handbuch der technischen Chemie*, 3rd ed., vol. iii., p. 193.

<sup>3</sup> For dye-wood extracts, especially extract of logwood, which is the most important technically, compare v. Cochenhausen, Muspratt's *Handbuch der technischen Chemie*, 3rd ed., vol. iii., p. 183; J. H. Soxhlet, *Chem. Zeit.*, 1890, 14, 667; L. Brühl, *ibid.*, 1890, 14, 767; Schreiner, *ibid.*, 1890, 14, 941.

<sup>4</sup> *Dingl. polyt. J.*, 1880, 235, 74.



provided they are performed with an extract solution of sp. gr. about 1.0035 and without an excess of the tin salt. Solutions of fermented extracts give a dark brown precipitate, those of unfermented extracts a pale violet precipitate, whilst extracts containing tannin yield a dirty, often yellow precipitate.

Finally, the ammonium sulphide reaction is very useful for the detection of tannin in logwood extracts. When a solution of 5 g. of the dry substance in 1 litre is treated with one-third its volume of yellow ammonium sulphide, a delicate brown, flocculent precipitate is produced in the case of pure extracts and the solution darkens, whilst extracts containing tannin yield a denser, pale grey, milky precipitate, and the solution instantly becomes lighter. Solutions of pure extracts containing about 1 g. per litre develop a slight dark turbidity, whilst those of extracts containing tannin give a pale, strongly turbid solution, and in a short time large, light flocks are produced (see section on "Leather" for extracts of tannin).

The valuation of logwood and of the logwood extracts (provided there is no adulteration with dyestuffs, such as chestnut extract, sumac extract, etc.) is ascertained by a dye-trial. Twenty grams of the wood or 5 g. of the extract are boiled with water in a porcelain basin on the water-bath, the liquid is poured through a linen cloth into a litre flask; the extraction is repeated until the solution is no longer coloured. Type solutions are prepared in the same way. Then as many pieces of wool, weighing 5 g., as there are dyeings to be performed are cut from thin woollen tissue and are placed for a few hours in a lukewarm solution of ammonium carbonate (5 g. per litre). The pieces are then washed carefully and, while still wet, are boiled in a mordant-bath containing, for each woollen piece, 10 c.c. of a solution of 8 g. of potassium bichromate and 2 g. of concentrated sulphuric acid per litre. All of the pieces are simultaneously introduced into the mordant-bath, which is slowly heated to boiling over a naked flame or, better, in a glycerol bath; the boiling is continued for half an hour. The pieces, shielded from light, are allowed to remain in the mordant-bath until it is cold, then they are washed, and dyed without being dried.

With each of the dyeing materials under examination, and also with the standard, two dyed samples, one light and the other darker, are prepared by using, for each woollen piece (5 g.), 10 c.c. and 20 c.c. of the dyeing solutions prepared as described above. The measured quantities of the dyeing solutions are diluted with the necessary amount of water in a porcelain beaker, the soaked woollen pieces are introduced, and the solutions are slowly heated in a glycerol bath to the boiling point and are kept at that temperature for half an hour. The pieces are then removed from the dye-bath, washed when cold, dried in the air, and compared with one another.

When it is desired to express numerically the value of a logwood extract in terms of a good extract, ten woollen pieces, each weighing 5 g., are dyed with quantities of a solution of a standard extract which decrease in arithmetical proportions, therefore, in the present case with

$$2 - 4 - 6 - 8 - 10 - 12 - 14 - 16 - 18 - 20 \text{ c.c.},$$

and that piece is noted which agrees in shades with a woollen piece dyed with 20 c.c. of the extract solution under examination.

For the simultaneous estimation of the dyeing power and the stage of oxidation of a logwood extract, J. Zubelin<sup>1</sup> recommends a process which depends on the use of oxidising and non-oxidising mordants. A type, consisting exclusively of hæmatoxylin, a certain amount of experience in the dyeing process, and accuracy in judging the dyed fabrics, are requisite to obtain good results.

The solutions which are employed contain 5 g. of extract (sp. gr. 1.26) in 1 litre of distilled water, and are modified as follows:—

1. The type is an extract (sp. gr. 1.26) of a good wood, and contains the dyestuff entirely in the form of hæmatoxylin.

2. An extract (sp. gr. 1.26) consisting almost entirely of hæmatein.

3. An extract (sp. gr. 1.26) composed one-half of hæmatoxylin and one-half of hæmatein.

4. An extract (sp. gr. 1.26), as in 1, but made into a vat with 20 per cent. of a tannin (sumac).

5. An extract (sp. gr. 1.26), as in 1, mixed with 0.5 per cent. of calcium carbonate.

*Experiment A.*—The wool to be dyed (100 g.) is mordanted with

3 g. of potassium bichromate,  
5 g. „ tartaric acid.

The wool then still retains an oxidising character, and gives an average shade after being dyed. The dyeings are performed for half an hour on the water-bath with 40 c.c. of the extract solutions (corresponding with 7 per cent. of extract, sp. gr. 1.26, calculated on the weight of wool), diluted with 400 c.c. of distilled water.

The colours possess the following character:—

1, with type 1, the characteristic bluish shade of hæmatoxylin.

2 is much darker than 1, and is nearly black.

3 lies between 1 and 2.

4 is weaker than 2, 3, and 1 (the same character would be obtained in the case of a non-oxidised extract mixed with other similar substances).

5 is darker than the colour produced by the type, in consequence of the oxidising action of the lime.

These trials prove that the oxidised extracts yield darker colours

<sup>1</sup> *Bull. Soc. Ind., Mulhouse*, 1898, 68, 257.

than the pure extracts, and that the latter produce darker colours than those made into a vat.

*Experiment B.*—The wool (100 g.) is soaked for two hours in a boiling-bath, as concentrated as possible, and containing

10 g. of alum,  
2.5 g. „ potassium bichromate,  
2.5 g. „ copper sulphate,  
2.5 g. „ tartaric acid.

It is then well washed and dyed as before, with the difference that only 3 per cent. of Campechy extract (calculated on the weight of the wool) is employed. The colours possess the following character:—

1. The pure hæmatoxylin produces the best colour.

2, 3, and 5 are lighter than 1.

4 is always weaker than 1.

When an unoxidised extract is required, an extract is selected which, according to the results of experiments A and B, gives results most nearly resembling those produced by the type.

When, however, an oxidised extract is required, preference is given to one which produces the darkest colour, as in experiment A.

*Experiment C.*—The dyeings are performed on cotton skeins, weighing about 8 g.

No. 1 like No. 1 in A and B.

No. 2 „ No. 2 in A and B.

No. 3 „ No. 2 made into a vat with 20 per cent. of water.

No. 4 „ No. 4 in A and B.

No. 5 „ No. 4 (plus an amount of calcium carbonate sufficient to neutralise the tannin).

No. 6 „ No. 5 in A and B.

The cotton must previously be washed thoroughly in boiling water. The Campechy solution, consisting of

300 c.c. of distilled water,  
100 c.c. „ the extract solution (as given above),

is warmed to 66—70°, the skeins are introduced, and are allowed to remain for two hours while the bath is cooling; then they are removed, squeezed, and placed for four to five minutes in a bath of copper sulphate (3 per cent. of the weight of the cotton).

No. 1 shows the grey shade of pure hæmatoxylin.

No. 2 is darker than 1.

No. 3 is still rather dark grey.

No. 4 is very poor (Campechy extract dyes cotton badly in the presence of an acid tannin).

No. 5 is darker than 4, because the tannin was previously neutralised, but is inferior to the type on account of the vatting.

No. 6 is the darkest; it is darker than the type but brighter than 2 and 3.

Extracts which have been mixed with tannins can also be recognised by their reddish grey shade.

By a comparison of the results of these three series of experiments it is always possible to pass judgment on a doubtful product.

With the object of lessening their cost, extracts of logwood, according to Brühl,<sup>1</sup> are mixed with molasses, dextrin, quebracho extract, chestnut extract, sumac extract, quercitron extract, sodium sulphate, and any other conceivable drugs; even the best qualities frequently contain not less than 20 per cent. of adulterants, whilst seconds may have 40 per cent., and thirds, as much as 70 per cent. In China and Japan in particular the third qualities are readily accepted.

Brühl finds that the European products are always adulterated with molasses, seldom less than 15 per cent., together with various amounts of chestnut, quebracho, and quercitron extracts, and frequently also sodium sulphate. Such adulteration with molasses (or dextrin) can be easily detected, according to Schweissinger,<sup>2</sup> by completely precipitating the solution of the extract with lead acetate, and examining the filtrate with Fehling's solution or by the polarimeter; pure logwood extract (either liquid or solid) does not contain any substance which is optically active or reduces Fehling's solution.

To detect chestnut extract,<sup>3</sup> 1 g. or 0.1 g. of the extract, previously dried at 100°, is treated with ether and the weight of the soluble portion determined. The residue which is insoluble in ether, is then completely extracted with absolute alcohol, and the weight of substance dissolved by this solvent is determined. By comparing these weights, with those obtained in the examination of a good, unadulterated logwood extract, it is possible to ascertain whether any adulteration has been practised. For example, 100 parts of extract gave

	Substances soluble in ether.	Substances soluble in alcohol.
Genuine extract . . .	87.1	14.3
Suspicious extract . . .	76.9	19.5

Chestnut extract is almost insoluble in ether, but is appreciably soluble in absolute alcohol; naturally, therefore, a suspicious extract will yield a larger amount of substance soluble in alcohol and a smaller amount soluble in ether than a genuine extract. The test can be amplified by the following experiment. Equal weights of the constituents, of the two preceding extracts, which are soluble in alcohol

<sup>1</sup> *Chem. Zeit.*, 1890, 14, 767.

<sup>2</sup> *Industrie Blätter*, 1887, 24, 337.

<sup>3</sup> *Dingl. polyt. J.*, 1868, 190, 242.

and in ether, must dye equal areas of calico in the same way, if they have the same composition. In the cases in question it will be found, therefore, that the ethereal extracts behave alike in the dye-trial whilst the alcoholic extracts produce very different results.

The substances mentioned above do not exhaust the list of adulterants of logwood extract; sand, clay, soil, sawdust, spent tan, etc., are not infrequently added to "improve" this widely employed extract.

The adulteration of logwood extract with glue, sugar by-products (molasses), and chestnut extract can be detected as follows:<sup>1</sup>—

First the water, nitrogen, and ash are estimated. Then an aqueous solution of the extract in question is decolorised by digesting at a gentle heat with coarsely powdered animal charcoal gradually added, and is filtered. Since the decolorisation of solutions of chestnut extract by animal charcoal is much more difficult to effect than that of solutions of pure logwood extract, the fact that comparatively great difficulty is experienced in decolorising the solution (a parallel experiment with unadulterated extract assists the judgment) is in itself a sign that further examination is necessary. If, therefore, by immediately heating the nearly colourless filtrate with Fehling's solution, a considerable amount of cuprous oxide is precipitated, the adulteration with chestnut extract is practically proved. If this is the case, the further examination of the behaviour of the original filtered (but not decolorised by animal charcoal) solution of the extract towards a solution of gelatine, which gives quite different results with logwood extract and chestnut extract separately, will only give useful information when the quantity of chestnut extract is the greater or at least exceeds 7 per cent. Adulteration with sugar by-products is proved when the extract solution, after being decolorised by animal charcoal and filtered, does not immediately give a precipitate, or only a very slight one (as is well known, molasses, particularly old molasses, frequently contain a small quantity of invert sugar), with Fehling's solution, but yields a considerable amount of cuprous oxide after inversion by dilute hydrochloric acid. Adulteration with glue is probable when the preceding phenomena are not observed and yet the amount of nitrogen considerably exceeds 1 per cent. In this case the addition of more than 8 per cent. of glue can be detected with greater certainty, but not conclusively, as follows:—Three to four grams of the powdered extract are twice or thrice treated with about 93 per cent. alcohol at the ordinary temperature, the residue is dissolved in warm water and precipitated by a solution of lead acetate. After the resulting blue precipitate has been removed, the excess of basic lead acetate in the filtrate is completely precipitated as lead carbonate by the addition of

<sup>1</sup> E. Donath, *Chem. Zeit.*, 1894, 18, 277.

sodium carbonate. The precipitate is filtered off, and a solution of tannin is added to the filtrate, whereby a precipitate or a distinct turbidity is produced if glue is present in the original extract.<sup>1</sup>

Donath found 0.81 per cent. of nitrogen and 33 per cent. of ash in a freshly prepared extract dried in a vacuum. Commercial unadulterated extracts gave

	I. (German manufacture).	II. (Belgian manufacture).
	Per cent.	Per cent.
Water . .	8.26	11.34
Nitrogen . .	0.78	0.58
Ash . .	6.39	4.99
		calculated on the dried substance.

The ash of each of these extracts contains a considerable quantity of alkali and a remarkably large amount of chloride and phosphate (even, as much as 7.81 per cent. of chlorine, and 2.12 per cent. of phosphoric oxide).

The considerably larger amount of ash in the commercial extracts, as compared with that in the pure extract, leads to the conclusion that this is conditioned by the so-called fermentation of the rasped logwood before it is employed in the production of extracts. (It is known that the process of "fermentation" usually consists in occasionally sprinkling the logwood with stale urine.)

The following preparations obtained from logwood or logwood extract will be mentioned briefly.

**Hematin** is placed on the market from Lyons and has properties<sup>2</sup> almost analogous to those of **Hæmatein**, prepared first by Erdmann;<sup>3</sup> it is probably obtained by extracting the fermented wood with ether.

**Indigo Substitute**, **Noir reduit** are violet blue liquids which are very extensively employed in the dyeing industry, and are prepared from logwood extract by means of potassium bichromate and sodium bisulphite. According to v. Cochenhausen<sup>4</sup> they may consist of the bisulphite compound of an oxidation product of haematoxylin, and a chromium salt. Also a few preparations seem to be obtained by dissolving the chromium lake, produced by treating logwood extract with potassium bichromate, in hydrochloric or oxalic acid.

**Direct Black**, **Imperial Black** or **Nigrosalin** are a mixture<sup>5</sup> of logwood extract and iron sulphate and copper sulphate, which is brought on the market in dark-coloured cakes, or as a dark brown

<sup>1</sup> Cf. also v. Cochenhausen, *Z. angew. Chem.*, 1904, 17, 877 et seq.

<sup>2</sup> E. Dollfus, *Dingl. polyt. J.*, 1880, 237, 464.

<sup>3</sup> *J. prakt. Chem.* 1882, [ii.], 26, 205.

<sup>4</sup> Muspratt's *Handbuch der technischen Chemie*, 3rd ed., vol. iii., p. 206.

<sup>5</sup> Breinl, *Dingl. polyt. J.*, 1887, 263, 487.

powder caking together in the air, or as a black pasty mass obtained by precipitating a decoction of logwood with a solution of iron sulphate and copper sulphate. The first-mentioned form of the commercial product is composed of two to six parts of logwood extract, two parts of iron sulphate, and one part of copper sulphate. Since the products supplied by different manufacturers never have the same composition, the shades developed by the same quantity of the dyestuff are never alike.<sup>1</sup> The shade is greenish when the copper sulphate predominates, and reddish violet, when much iron sulphate is present. All possible black shades can be produced, therefore, by varying the quantities of these two salts.

A preparation placed on the market under the name **Direct Black for Cotton** consists of a brown viscous mass, and is composed, according to v. Cochenhausen, of about 50 per cent. of water, 45 per cent. of a substance soluble in alcohol and ether (hæmatoxylin and hæmatein), and 3.5 to 7 per cent. of copper sulphate.

**New Printing Blacks SS, NR, NRG** (*Leonhardt*)<sup>2</sup> are logwood extracts which have a strong odour of acetic acid, and, mixed with sodium chlorate, can be employed directly for printing cotton without the addition of chromium acetate.

#### General Remarks on the Estimation of Dye-wood Extracts.

Liquid or solid extracts of dye-woods are still extensively employed in dyeing and printing as substitutes for dye-wood decoctions prepared on the spot. In spite of the additional expense of manufacturing the extract it is economical to employ extracts of dye-woods, which are always cheaper in consequence of the considerable saving in the cost of freight. It is more advantageous for the printer, who must always work with concentrated infusions, to employ extracts which are readily converted into concentrated infusions by solution. Also in many cases it is almost compulsory for the dyer to use extracts, especially when the dye-bath is required, at a concentration which can only be attained by a lavish consumption of material in the usual process of boiling. Conversely there are occasions on which the woods cannot be replaced by extracts. Thus in dyeing wool purer and better colours are obtained from decoctions of the wood than from solutions of the extracts. Decoctions of dye-woods, particularly of logwood, also produce colours which are faster to air than those obtained by means of extracts. For many purposes—for example, for “topping” blue on cotton (as substitute for vat-blue)—a freshly prepared decoction of logwood cannot be replaced by extracts. Generally, however, in cotton-dyeing with logwood, fustic, and quercitron the employment of extracts is more advantageous than that of the chips.

<sup>1</sup> v. Cochenhausen, *loc. cit.*, p. 207.

<sup>2</sup> *Rev. Gen. Mat. Col.*, 1898, 2, 459.

Deleterious effects are frequently produced in dyeing processes by resinous particles which are present in the extracts of boiled-out woods—in contradistinction to the ordinary dye-wood decoctions—and develop small dark spots on the dyed material.<sup>1</sup>

The following criteria are applied by Schreiner<sup>2</sup> to the valuation of a dye-wood extract, particularly of logwood extract, which is the substance most frequently requiring examination: 1. Percentage of dyestuff; 2. Addition of foreign dyestuffs and tannins; 3. Addition of weighting materials; 4. Fermentation and reaction (the latter has been described on p. 1153).

In consequence of the great similarity in the behaviour of the dyestuffs of dye-woods (particularly of haematoxylin and hæmatein) and of tannins, Schreiner has applied the so-called "Viennese gravimetric process of estimating tannins" published by Weiss,<sup>3</sup> to the estimation of dye-wood extracts.

Fifty grams of the ground dye-wood are completely extracted with an alkali in a specially constructed, very convenient extraction apparatus, and the solution is diluted to 1 litre and filtered. A portion of the filtrate is allowed to flow through hide-powder in a special filtering apparatus<sup>4</sup> with the necessary precautions. The hide-powder for this purpose must be of the purest quality and in a woolly form. The filtrate in a successful experiment is absolutely colourless, and remains so even after the addition of ammonium hydroxide, since it contains only substances devoid of dyeing or tanning properties. Then 100 c.c. of this filtrate and also of the original solution are evaporated on the water-bath, and the residues are dried in an air-bath at 100° until the weights are constant. The difference of the two weights represents the amount of dyestuff.

In dealing with extracts a solution is prepared containing about 10 g. of the dried substance in 1 litre. After the solution has been made up to volume at the ordinary temperature, it is warmed on the water-bath at 50°, filtered, if necessary, with the addition of kaolin, and the clear solution is treated as above. In addition, 1 to 2 g. of the extract are dried at 100° in a platinum vessel, to determine the water, and the dry residue is incinerated to determine the mineral constituents.

The content of insoluble matter is calculated from the difference of the weight of the dry substance and the sum of the weights of the dyestuffs and non-dyestuffs, that is, of the total soluble matter. The amount of mineral matter is subtracted from that of the non-dyestuffs. (The occurrence of mechanical impurities in the "insoluble" matter is extremely rare, but when it happens it is easily seen.)

<sup>1</sup> v. Cochenhausen, *loc. cit.*, p. 186.  
*Chem. Zeit.*, 1890, 14, 961.

<sup>3</sup> Cf. Gerber, 1895, 21, 63.

<sup>4</sup> *Z. angew. Chem.*, 1888, 1, 717.



Schreiner gives the following examples:—

FRESH LOGWOOD.					
	I.	II.	III.	IV.	
				Fresh.	Fermented.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Dyestuffs . . . . .	12.06	10.56	8.16	9.70	9.26
Non-dyestuffs . . . . .	2.22	1.72	1.04	2.05	1.10
Water . . . . .	10.86	12.80	10.80	10.02	16.00

EXTRACT: LIQUID, SPEC. GRAV. 1.26.					
	I.	II.	III.	IV.	V.
				Solid.	
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Dyestuffs . . . . .	52.52	41.39	33.52	79.77	54.36
Non-dyestuffs . . . . .	6.06	11.91	14.39	9.03	18.14
Insoluble at 50° . . . . .	0.45	2.87	6.99	1.05	9.20
Ash . . . . .	0.14	1.81	3.47	0.22	6.04
Water . . . . .	40.83	42.02	41.63	9.88	12.26

The extract analyses quoted are compiled from extreme cases: I. and IV. are normal extracts of a good wood; II. contains an addition of about 20 per cent.; III. of about 10 per cent. of an extractive substance (syrup) containing a considerable amount of lime; V. contains an addition of extractive substances and salts (sodium sulphate).

A glance at the examples quoted suffices to show the importance of analysis when buying dye-woods, particularly when it is mentioned that I., II., and III. are woods of the same brand. Unfortunately, the extract manufacturer is only rarely in a position to be able to procure in advance a truly average sample of the wood. Also the content of non-dyestuffs is of considerable importance, especially for wool-dyeing, since the fermentation proceeds more easily and thoroughly the greater the amount of non-dyestuffs. The process of fermentation and the accompanying partial formation of volatile products are conditioned by these substances, and through their activity the logwood dyestuff is brought to the surface of the wooden particles, and is thus given the opportunity of combining with oxygen.

The only fault of these new methods of Schreiner is that the dyestuffs and any tannins present cannot be estimated separately. This disadvantage becomes of considerably less importance, however, from the fact that for the purposes to which such dyestuff extracts containing tannin are chiefly applied, especially in cotton black dyeing, the

presence of the tannin, except so far as the cost of the product is concerned, is scarcely worthy of notice.

### Archil Preparations.

The raw materials are different kinds of lichens, preferably *Lecanora* and *Rocella tinctoria*, which are known by the common name, Plant Archil; the best kinds are obtained from Angola, Ceylon, Madagascar, Mozambique, and Zanzibar. "Earth Archil," which is largely contaminated with mineral matter, serves chiefly for the preparation of litmus. The most important constituent of these lichens is orcinol, which forms dyestuffs and is produced by the decomposition of the lichen acids during the chemical treatment of the lichens. It is converted by the action of ammonium hydroxide (stale urine, etc.) and air into orcein, a magnificent red, crystalline dyestuff. In addition, there are produced, according to Zulkowski and Peters,<sup>1</sup> a yellow, crystalline dyestuff, and an amorphous dyestuff which is very similar to, and is probably identical with, litmus. Solutions of pure orcein in alcohol, acetic acid, and acetone have a splendid carmine colour, and acquire a magnificent bluish violet colour by the addition of ammonium hydroxide and fixed alkalis. The dyeing power of pure orcein is 150 to 200 times that of archil extract. Orcinol develops a deep violet coloration with a solution of calcium hypochlorite, and on warming with a little chloroform in alkaline solution, forms a purplish red liquid, which shows an intense greenish yellow fluorescence after dilution with water (the sodium salt of homofluorescein).<sup>2</sup> This sensitive reaction is employed for the recognition of lichens containing orcinol (and therefore suitable for the manufacture of archil extract or litmus). A piece of the lichen is boiled for a short time with dilute potassium hydroxide, the clear liquid is poured off and warmed, after the addition of a drop of chloroform, for ten minutes on the water-bath, and is then diluted with water. If the lichen contains orcinol or substances yielding orcinol, a greenish yellow fluorescence is distinctly perceptible.<sup>3</sup>

The amount of dye-forming lichen acids in lichens, which varies from about 2 to 12 per cent., is estimated by Stenhouse's process<sup>4</sup> as follows:—The lichen (100 g.) is rapidly extracted with milk of lime (if the extraction is too prolonged, more than 15 to 30 minutes, a portion of the lichen acids is converted into orcinol, and therefore is not precipitated subsequently by the acetic acid); the extract, after being filtered, is treated with acetic acid, and the precipitate is collected on a tared filter, dried at the ordinary temperature, and weighed. The

<sup>1</sup> *Monatsh.*, 1890, II, 227.

<sup>2</sup> Schwarz, *Ber.*, 1880, 13, 543.

<sup>3</sup> v. Cochenhausen, Muspratt's *Handbuch der technischen Chemie*, 3rd ed., vol. iii., p. 230.

<sup>4</sup> *J. prakt. Chem.* 1848, 45, 180; *Annalen*, 1848, 68, 55.

method is a good one, but is tedious. A quicker process is the following:—

One hundred grains of the lichen, cut into very small pieces, are twice macerated with a dilute solution of sodium hydroxide, and are thereby exhaustively extracted. After filtration, the extract is treated with a standard solution of sodium hypochlorite from a burette. At the instant when the hypochlorite enters the alkaline lichen extract, a blood-red coloration is produced, which disappears after 1 to 2 minutes and the liquid acquires a deep yellow colour. More hypochlorite is now added, and the operation is repeated with careful shaking so long as any further addition still produces a red colour (thus indicating that unoxidised, dye-forming material is still present).<sup>1</sup>

To a very small extent, Archil preparations (see below) or orcein dyestuffs are employed in producing violet colours (without mordants) on wool and silk (never on vegetable fibres), and brown and fancy colours on wool (and to a smaller extent on silk). Archil preparations have been displaced to some extent by various coal tar dyestuffs.

The chief Archil preparations occurring commercially are Archil in paste, Archil extract, French purple, and Cudbear.

The simplest preparation is that of **Archil in paste**, also known shortly as Archil, which is made by treating and stirring the finely divided lichens for a few weeks with a solution of ammonium hydroxide with free access of air. By shortening the time of preparation, a redder Archil is obtained, in other cases a more violet. A distinction is drawn between Plant Archil and Earth Archil.

**Archil Extract**—As the result of its method of preparation, archil in paste contains, in addition to the orcein, impurities, such as the ligneous portions of the lichens, undecomposed lichen acids, and mineral matter, which are undesirable for certain of its applications in dyeing. Consequently, the lichen acids are dissolved by treatment with milk of lime,<sup>2</sup> and the clear solution is either directly treated with ammonium hydroxide and exposed to the air, or the lichen acids are first precipitated by hydrochloric or sulphuric acid, and are then dissolved in ammonium hydroxide and exposed to the air. According to these different methods of treatment and the varying degrees of concentration and purity resulting therefrom, the archil extracts are called simple, double, concentrated, or archil carmine.

**French Purple** (Archil Violet) is prepared as follows:<sup>3</sup>—The lichen acids are first extracted as usual by milk of lime and are precipitated by an acid; they are then dissolved in ammonium hydroxide and exposed to the air at the ordinary temperature until, not a violet, but a cherry-red colour is produced. After being boiled for some time,

<sup>1</sup> Cf. also H. E. Watt, *J. Soc. Chem. Ind.*, 1908, 27, 612.

<sup>2</sup> *Jahresber. d. Chem. Techn.*, 1859, 490.

<sup>3</sup> Spence and Guinon, *ibid.*, 1859, 492.

the liquid is placed, to a depth of 5 to 6 cm., in large flat dishes, and kept at 70—75° until it has become purplish violet. The solid dye-stuff is precipitated from this solution by sulphuric acid or a solution of calcium chloride. In the latter case, a calcium lake, insoluble in water, is produced, which before being employed in dyeing, must be brought into solution by treating a suspension of the finely divided lake in water with ammonium carbonate or with oxalic acid or sulphuric acid and the subsequent addition of ammonium hydroxide.

**Cudbear** (Red Indigo), like French purple, is a solid mass which is obtained by drying Archil extract, or from plant or earth archil. The commercial brands are Cudbear O, I, II, extra, fine, violet, red violet, blue violet, and red.<sup>1</sup> Orchellin is a product which is very rich in dyestuff.

**Archil Carmin** and **Archil Purple** contain archil dyestuffs in a state of great purity.

As mentioned above, a blue violet and a red archil occur commercially, the different colour shades being due to the duration of the action of ammonium hydroxide and air.

By treating the former with a small quantity of potassium ferricyanide it acquires all the properties of red archil. French purple differs from archil in that the latter is coloured red by hydrochloric or sulphuric acid, whilst the violet shade of French purple is only slightly reddened even by moderately strong hydrochloric or sulphuric acid. On the other hand, the magnificent violet solution obtained by dissolving French purple in moderately concentrated sodium hydroxide becomes red when it is saturated with hydrochloric acid.

French purple and aniline violet differ in that the former is only slightly reddened by moderately strong hydrochloric acid, but becomes decidedly red if treated with sodium hydroxide before being acidified, whilst aniline violet yields with hydrochloric acid a blue colour, which is so much the purer the more concentrated the acid.<sup>2</sup>

A dye-trial is the only method of estimating the quality of archil preparations. A weighed or measured piece of wool is placed in a bath containing 1 g. of the archil preparation in 500 c.c. of water, which is boiled for half an hour. The wool, after being washed and dried, is compared with a sample dyed by a good quality of archil.

The method given by v. Cochenhausen<sup>3</sup> is more exact. Five grams of the archil or of the archil preparation under examination are dissolved in 1 litre of water; 50 c.c. of this solution are employed in dyeing every 1 g. of wool. The dye-bath contains 10 per cent. (of the weight of the wool) of alum or 10 per cent. of alum and 2 per cent.

<sup>1</sup> v. Cochenhausen, Muspratt's *Handbuch der technischen Chemie*, 3rd ed., vol. iii., p. 233.

<sup>2</sup> Mierzinski, *Die Erd-, Mineral- u. Lackfarben*, 1881, p. 354.

<sup>3</sup> *Loc. cit.*, p. 234.

of tartar. The value of an archil, in comparison with that of a standard preparation, can be approximately expressed numerically by comparing the dyed sample with a scale of 1 g. samples dyed under the same conditions with:—

5—10—15—20—25—30—35—40—45—50 c.c.

of a solution of 5 g. of the standard preparation in 1 litre of water.<sup>1</sup>

Leeshing<sup>2</sup> detects adulteration of an archil extract with extract of logwood or Brazil wood as follows:—Fifty drops of the extract are diluted with about 100 c.c. of water, the liquid is faintly acidified with acetic acid, treated with fifty drops of a solution of stannous chloride (1:2), and heated to boiling. A pure archil solution is at once almost decolorised, whilst a blue-grey or a red solution is obtained if extract of logwood or of Brazil wood respectively is present; the blue-grey to grey colour is produced in the presence of at least 3 to 4 per cent. of logwood extract.

For the detection and estimation of magenta in archil and cudbear, Rawson<sup>3</sup> has described a very delicate process which indicates even 1 part in 100,000 parts of cudbear:—One to two grams of cudbear (or a corresponding amount of the archil liquid) are boiled with 50 c.c. of alcohol, diluted with 100 c.c. of water, treated with 15 to 20 c.c. of a strong solution of basic lead acetate (sp. gr. 1.25), and, after being stirred, with an equal quantity of strong ammonium hydroxide. The precipitate is collected and washed, if it is desired to estimate the magenta quantitatively, with a mixture of one part of ammonium hydroxide, five parts of alcohol, and ten parts of water. The filtrate from pure cudbear is colourless, but if magenta is present the filtrate is colourless or rose-coloured according to the quantity of ammonium hydroxide added. On acidifying with acetic acid the liquid becomes red if magenta is present. In addition Rawson employs the following colorimetric method for the approximately quantitative estimation of the detected magenta. A pure magenta solution, containing acetic acid, is prepared such that 0.01 g. of magenta is present per litre. The solution to be examined is diluted to 250 c.c. and an aliquot portion is diluted to 100 c.c. and placed in one tube of the colorimeter. The standard magenta solution is run from a burette into the second tube of the colorimeter, until the intensities of the colours of the liquids in the two tubes are equal.

A similar but less sensitive method of detecting magenta is described by Schweissinger.<sup>4</sup> It depends on the fact that the archil dyestuff is completely precipitated in half an hour by lead acetate in

<sup>1</sup> Cf. also Heermann, *Mitt. K. Materialprüfungsamt; Gross-Lichterfelde West*, 1910, p. 41.

<sup>2</sup> *Chem. Gazette*, 1855, 13, 219. <sup>3</sup> *Chem. News*, 1888, 57, 165.

<sup>4</sup> *Pharm. Centr.*, 1887, 95.

neutral or faintly alkaline solution, whilst the magenta remains in solution and can be detected in the filtrate. The solution obtained by extracting 0.25 g. of archil with alcohol is evaporated on the water-bath and the residue is dissolved in 50 c.c. of water, precipitated by 10 c.c. of lead acetate and filtered after half an hour.

Kertesz<sup>1</sup> detects magenta or acid magenta in archil extract by repeatedly boiling a small quantity of the extract with a fairly large volume of water, and filtering until the solution is quite clear. A portion of this solution is well mixed with benzaldehyde (oil of bitter almonds) in a test tube, and then stannous chloride and hydrochloric acid are added. After being thoroughly shaken and kept for a few minutes the liquid separates into two layers, the lower of which has a magenta-red colour if magenta is present but otherwise is colourless. By this means one part of acid magenta can be detected in one thousand parts of archil extract.

By Liebmann and Studer's method<sup>2</sup> it is also possible at the same time to ascertain whether the adulterant is magenta or acid magenta (*cf.* p. 1000). A cold solution of one part of cudbear in one hundred parts of water is saturated with sulphur dioxide. By this means the greatest portion of the archil dyestuff is precipitated, whilst the magentas remain in solution and produce a violet coloration in the liquid after the addition of acetone. If the presence of magenta dyestuffs has been thus proved, cotton, mordanted with tannin and tartar emetic, is dyed in the solution which has been saturated with sulphur dioxide and filtered; the magenta only (not the acid magenta) is fixed on the fibre.

Brein<sup>3</sup> has confirmed the trustworthiness of the preceding process, and has published a detailed table of the reactions of archil and of the coal tar dyestuffs which are used as adulterants, with stannous chloride and hydrochloric acid, lead acetate (sp. gr. 1.26), sodium chloride, sodium hydroxide, concentrated sulphuric acid, hydrochloric acid, and nitric acid.

## 2. YELLOW DYES

**Quercitron** is brought on the market in the form of a yellowish or fawn-coloured powder, and consists of the ground bark, freed from the epidermis, of the *Quercus tinctoria*, which is indigenous in America but is also cultivated in France and South Germany. The finer and the yellower the powder, so much the better is the quality. Quercitrin, the light yellow dyestuff in the bark, is decomposed by dilute acids into isodulcitol and quercetin.

The reddish brown decoction of the bark does not keep, and therefore should be prepared only when required for immediate use. The

<sup>1</sup> *Dingl. polyt. J.*, 1885, 256, 281.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1886, 5, 287.

<sup>3</sup> *Mitt. techn.-Gew. Mus. Wien.*, 1887, p. 37; *J. Soc. Dyers and Col.*, 1888, 4, 46.

commercial products are **Quercitron Extract**, sp. gr. 1.07 to 1.16, the solid residue obtained by evaporating this extract, and also **Flavin** and **Quercetin**. According to Ganswindt, flavin contains an acid, and quercetin a basic, dyeing principle. Flavin, which has been manufactured hitherto only in North America, is prepared as follows, according to Soxhlet:<sup>1</sup>—One thousand kilos of the bark are extracted with 2.5 cbm. of water in closed vessels; the quercitrin is more readily dissolved if the water contains 5 to 7 per cent. (of the weight of the bark) of crystallised sodium carbonate, or a corresponding quantity of borax or ammonium hydroxide. An alternative process is to dilute quercitron extract to the corresponding extent with water, and to treat the boiling solution with alkaline substances and to heat it at the boiling point for one hour (an operation which exercises the greatest influence on the quality of the product) with a diluted mixture of two parts of sulphuric acid and three parts of hydrochloric acid, which mixture may contain with advantage a definite amount of metallic tin in solution. The operation results in a fairly smooth decomposition of the quercitrin into quercetin and isodulcitol. When the boiling is finished the liquid is passed through a filter-press and the product on the filter is dried. The yield amounts only to 4 to 10 per cent. of flavin of very variable quality. Good flavin has about twelve to eighteen times the dyeing value of quercitron bark and quercitron extract, produces much purer shades, and also does not contain tannin.

*Quercetine industrielle* is prepared in exactly the converse way, by extracting the bark or treating the diluted extract with a mixture of sulphuric and hydrochloric acids and precipitating the filtrate with alkalis. By treating flavin with concentrated nitric acid (36° Bé.) a product is obtained which is even stronger than this, and gives other dyeing effects.

Quercitron produces a beautiful colour and has a strong dyeing power (three times as great as that of fustic and eight times that of weld).

It is still employed for dyeing wool and cotton, for the production of mixed colours, and for shading logwood black.

Good quercitron bark is pale yellow. The appearance is to some extent a criterion of the quality, but in addition the amount of water and of ash (sign of adulteration with clay or sand) in the bark or extract is estimated. The extract is adulterated with dextrin and glue; flavin frequently contains as much as 25 per cent. of anhydrous sodium sulphate or of sodium chloride, and feels damp in the latter case. Soxhlet states (*loc. cit.*) that good flavin should not be completely soluble in boiling water, the solution should be turbid and pale; a precipitate should not be produced by the addition of aluminium sulphate, but the colour of

<sup>1</sup> *Chem. Zeit.*, 1890, 13, 1345.

the liquid should instantly change to bright yellow. An aqueous solution of flavin, kept in an open vessel, loses all its dyeing power in a few days.

The amount of dyestuff in the bark or the extract and also adulteration of the latter with dextrin, glue, etc., or of the former with fustic, are ascertained by dye-trials.<sup>1</sup>

Wool is soaked in 1.5 per cent. of stannous chloride and 3 per cent. of oxalic acid, and after being washed is dyed with 20 c.c. (for every 1 g. of wool) of a solution of 10 g. of quercitron extract or the corresponding quantity of quercitron bark in 1 litre of water. The amount of dyestuff, in comparison with pure flavin or a good extract or a good bark, can be approximately expressed numerically by dyeing 1 g. pieces of woollen skein with 1, 2, 3, . . . . 8, 9, 10, . . . 18, 19, 20 c.c. of a solution of the standard dyestuff prepared in the same way.

**Fustic**, which is usually placed on the market in the form of billets, consists of the very hard, glistening yellow stem of the *Morus tinctoria*, which flourishes in the West Indies, Brazil, and Mexico. The best kind of fustic comes from Cuba, whilst a very common commercial article is Tampico fustic; in addition to these, the Brazil, Porto Rica, and Jamaica fustics are well known. Fustic should have a bright citron yellow colour and is frequently seamed by red veins. It is employed either as a powder or in chips or as an extract (Cuba extract). It contains the calcium compound of morin, which is colourless itself, and maclurin. Owing to the presence of the latter, fustic is also used for producing black dyes. Fustic must be extracted with steam, and a little gelatin must be added to the dye-bath since both operations exercise a beneficial influence on the brightness and beauty of the colour. The effect of the gelatin—about 5 per cent. of the fustic employed—is to precipitate the maclurin, which produces turbid brownish colours by too prolonged boiling in the dye-bath. On precisely similar grounds the quercitron dye-bath is treated with glue or alum. J. Nowak, Söhne, and K. Benda of Smichow-Prague<sup>2</sup> manufacture a product under the name "morin," which is obtained by extracting rasped fustic with boiling water, and 2 per cent. of sodium carbonate and concentrating the solution until its sp. gr. is 1.041.

**Santiago New Yellows E and K** are fustic preparations which are obtained by a new process by the firm of G. Eberle & Co. (Stuttgart). The brand E is wholly oxidised, and is particularly suitable for dyeing wool and cotton in pale shades; the brand K is only partly oxidised, and is therefore to be recommended for use with oxidising mordants.

The condensation products of fustic extract and diazo compounds,

<sup>1</sup> v. Cochenhausen Muspratt's, *Handbuch der technischen Chemie*, 3rd ed., vol. iii., p. 259.

<sup>2</sup> D. R.-P., 2552; *Ber.*, 1878, 11, 1951.



which are known as **Patent Fustic**, are also used. Chromed wool is dyed yellow-brown by them.

v. Cochenhausen<sup>1</sup> estimates the dyestuff in the wood or extract as follows:—Wool is soaked for three-quarters of an hour in a solution containing 10 per cent. of alum, and is washed; it is then dyed at 80—90° for three-quarters of an hour in a solution of 10 g. of fustic extract or a decoction of a corresponding quantity of fustic in 1000 c.c. of water, 10 c.c. of the solution being taken for every 1 g. of wool. The amount of dyestuff, in comparison with that in a good extract or wood, can be approximately expressed numerically by dyeing ten samples of mordanted woollen skein with 1, 2, 3, . . . 8, 9, 10 c.c. of a solution, prepared in the same way, of the standard extract or wood. Fustic in conjunction with other dye-woods is employed in wool and cotton dyeing for the production of mixed colours (brown, olive) and for shading logwood black.

**Weld** consists of the dried stalks and leaves of the odourless plant, *Reseda luteola*, which grows wild and is also cultivated. The more rapidly the weld is dried the more pronounced is its dyeing power. It produces very beautiful, fast colours particularly in combination with alum on wool and silk, but has nevertheless been replaced by the much more powerful quercitron. The well-known weld-green is, however, produced on silk by adding indigo-carmin and sulphuric acid to the weld dye-bath.

Welds are distinguished as French, German, and English, the last being of little value.

**Persian berries** are the unripe fruit, gathered while still green, of a few species of the *Rhamnus*, and have a greenish yellow colour when dried. The berries should not be used immediately after they have been gathered, nor when they are more than a year old, since in both cases the dyestuff is not at all strong. The aqueous decoction of Persian berries has a greenish brown colour which is changed to orange by alkalis. It produces a beautiful and fairly permanent yellow, which finds application in paper manufacture. Extract of Persian berries is extensively employed in calico printing for the preparation of Steam Orange, Green and Olive.

Blackened Persian berries should not be willingly accepted, because the colour indicates that the berries have been stored while damp or have been gathered when ripe. The value of Persian berries is estimated by dye-trials in the manner described under Fustic.

**Annatto** is a dyestuff obtained from the fruit of *Bixa orellana*; almost its only use at the present day is for colouring butter and varnishes. It is brought on the market in the form of a plastic red paste, which is superficially brownish red, has an unpleasant odour,

<sup>1</sup> Muspratt's *Handbuch der technischen Chemie*, 3rd ed., vol. iii., p. 262.

and may contain many impurities such as leaves, starch, pieces of wood gum, brick dust, colcathar, and bolus.

On account of the very variable percentage of water all tests of annatto must be performed with samples dried at 100°. The ash is estimated by calcining 5 g. of the dried annatto. Good qualities contain 8 to 13 per cent. of ash. A percentage of ash exceeding 15 is conclusive proof of adulteration with mineral matter; this can also be easily detected by grinding the annatto with water. Comparative dye-trials of annatto are conveniently performed as follows.<sup>1</sup> A bath containing

	For cotton.	For silk.
Annatto, dried at 100° and powdered	5 g.	0.5 g.
Tartar	10 g.	1.0 g.
Distilled water	200 g.	100 g.

is heated to boiling, and in it is placed a skein consisting of 12 g. of cotton and 2 g. of white silk. After boiling for fifteen minutes the source of heat is removed; after an hour each skein is removed from its bath, wrung out, washed in a large quantity of water, and allowed to dry in the shade. The depths of the shades of the individual skeins are compared. The best quality of annatto is that which most nearly produces the same shade as the annatto which has been selected as the type.

Annatto contains two dyestuffs, bixin and orellin. The former yields with concentrated sulphuric acid a deep blue colour, untinged with green or brown. Impure or spoilt annatto, on the other hand, produces a greenish or blackish colour.

### 3. RED DYES

**Cochineal** has been almost entirely superseded by artificial dyestuffs, but is still employed to some extent in dyeing wool (*e.g.* the scarlet cloth for the British army) and silk. Cochineal is an insect, *Coccus cacti*, which lives on cactus leaves, is bred mostly in plantations, and multiplies with extraordinary rapidity. Cochineal (mesteque) bred in plantations is much superior to the wood or field cochineal (*silvestra*). The method of treating the gathered insects also has the greatest effect on the quality. The best quality is obtained by exposing the gathered insects to direct sunlight, whereby they are quickly killed and the prized silver-grey colour (mesteque jaspeada) is produced. Dark brown or blackish brown cochineal (mesteque negra) is obtained by drying the insects in ovens on hot plates or earthen pans. The worst (brownish red) quality (mesteque renegrída) is produced when the collected insects are killed by rapid immersion in

<sup>1</sup> Mierzinski, *Die Erd-, Mineral- und Lackfarben*, 1881, 344.

hot water and are then allowed to dry slowly. The quality is also largely dependent on the time at which the insects are collected. The first brood, in which merely the pregnant females are collected, is the best; in the second gathering young insects also are taken, and in the third harvest, which must be gathered hastily and at the right moment on account of the approaching rainy season, many very young insects together with much foreign matter, are found.

The cochineal insect is bred in Mexico, South America, Algiers, the Canary Isles, and Java. Four main kinds are placed on the market; Vera Cruz, Honduras, Canary, and Java-cochineal.

According to Mierzinski<sup>1</sup> a good cochineal consists of blackish or bluish dark red insects, which have a silvery-grey appearance, are 2 to 2.5 mm. long, and semi-oval in shape; they are easily friable, and produce a bitter and slightly astringent taste. The slightly arched back shows a series of parallel furrows, and the under-surface is flat or concave. The ground insects form a fine dark red powder. After twelve to fifteen hours' immersion in water, the insects swell up and then the proboscis and also the feet on the under-side can be seen through the microscope. At the same time the water acquires an intense crimson red colour. Spurious cochineal is converted into a broth by this treatment, and the gum by which the artificial mass is cemented, becomes obvious.

Various commercial preparations are produced from cochineal on a manufacturing scale:—

1. *Cake Cochineal* is cochineal stamped into cakes, containing about 80 per cent. of the dyestuff of ordinary cochineal.

2. *Carmin Lake* (Florentine lake, Munich lake, Vienna lake).—An alkaline decoction of cochineal is precipitated by alum or by alum and stannous chloride. The carmine lakes are employed as water- and oil-colours in tapestry printing and in lithographic printing.

3. *Carmin*.—The aqueous extract of finely ground cochineal, with or without the addition of sodium carbonate, is precipitated by a weak acid or an acid salt. Details of the different processes are trade secrets. v. Sochenhausen<sup>2</sup> describes the principles of the various methods, of which the following is given here: 500 g. of the finely powdered cochineal are boiled for a quarter of an hour with thirty times the weight of distilled water, 30 g. of tartar are added, the boiling is continued for another ten minutes, then 15 g. of alum are added, and the mixture is boiled once again for two minutes. The clarified liquid is allowed to remain in flat glass vessels. The separated carmin is washed with water and dried in the shade.

It is probable that carmin is not an ordinary compound of a

<sup>1</sup> *Die Erd-, Mineral- und Lackfarben*, 1881, p. 151.

<sup>2</sup> Muspratt's *Handbuch der technischen Chemie*, 3rd ed., vol. iii., p. 247.

dyestuff and alumina, but consists of an aluminium-calcium albuminate of the carmin dyestuff.

4. *Ammoniacal Cochineal*.—One part of ground cochineal is submitted to the action of three parts of ammonium hydroxide for four weeks in the complete absence of air, then 0.4 part of freshly precipitated aluminium hydroxide is added, and the mixture is evaporated in a copper boiler until the odour of ammonia is no longer perceptible. It is sold in the form of small tablets and as a paste.

On account of its high price cochineal is very frequently liable to be adulterated, especially with particles of lead, lead filings, sand, and the like. The impurities mentioned are easily detected by grinding about 0.5 g. of cochineal in a porcelain mortar and triturating it with water. Frequently also the dyestuff of the (unground) cochineal is extracted, and the cochineal grains are then placed in a solution of extract of Brazil wood, the artificially recoloured cochineal being then shaken with talc or white lead in order to produce the appearance of the natural, good (silvery grey) cochineal. The latter procedure is often practised on the worst quality of cochineal (*mesteque renegrada*) (see above) for the same purpose. A white powder comes off when such cochineal is rubbed between the hands, and blackening is produced by hydrogen sulphide if white lead has been used. Lime water does not change the colour of the aqueous extract of such cochineal, whilst it converts the colour of a genuine cochineal into violet. Adulteration is also carried out with powdered archil and dragon's blood (see below). An abnormal percentage of ash points to adulteration with red dyestuff lakes.

*Adulteration of Cochineal Carmin with the Lakes of Coal tar Dyestuffs*.<sup>1</sup>—The addition of such is detected by the incomplete solubility of the adulterated product in ammonium hydroxide as well as by an estimation of the ash.

Genuine cochineal carmin dissolves completely in ammonium hydroxide; the lakes of coal tar dyestuffs do not. The adulteration can be detected by merely heating carefully a small quantity of genuine carmin in one porcelain crucible and about the same amount of the sample under examination in a second crucible. The odour of the decomposing genuine carmin resembles that of protein substances decomposing by heating, whilst from the odour of the adulterated products in question some idea can at once be obtained of the nature of the adulterant; eosin lake produces an appreciable odour of bromine by heating, peony lake the odour of phenol, and the baryta lake of Biebrich scarlet an equally characteristic odour, which is instantly distinguished from that of the genuine carmin.

After complete combustion adulterated samples leave a greater

<sup>1</sup> E. Donath, *Färber-Zeit.*, 1894-95, 6, 174.

residue of ash, by the qualitative examination of which further information can be obtained.

The valuation of cochineal can be determined colorimetrically by dye-trials, or by the volumetric estimation of the amount of dyestuff.

(a) *Colorimetric Estimation*.—One gram of cochineal is exhaustively extracted with boiling water, a few drops of alkali are added if the solution has an orange tinge, and the solution is examined by a colorimeter, Houton-Labillardière's, Salleron's, Collardeau's, or Müller's, or the simplest plan is to use two adjacent burettes of the same dimensions, one of which contains the standard solution and the other the liquid under examination, and to dilute the more strongly coloured solution until the intensities of both are the same.

(b) *Dye-trials*.—According to v. Cochenhausen,<sup>1</sup> 1 g. of powdered cochineal is repeatedly boiled with water and the combined extracts are diluted to 1 litre with water. For every 1 g. of woollen skein used in the dyeing, 100 c.c. of this solution are taken, diluted with water, and treated with 3 per cent. of oxalic acid and 1.5 per cent. of stannous chloride (calculated on the weight of the wool). In the dye-bath thus prepared, the skein, after previously being thoroughly soaked, is slowly heated until after half an hour the bath boils; the boiling is continued for yet another half-hour. Also, the wool can be previously soaked with stannous chloride and oxalic acid, and after being washed be dyed in a fresh bath with the same quantity of the cochineal decoction. If it is desired to compare the cochineal under examination with a standard sample, a decoction of 1 g. of the latter is prepared in the manner described, and 1 g. pieces of wool are dyed, with the addition of oxalic acid and stannous chloride, with 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 c.c. of the decoction. By means of the scale thus obtained the value of a cochineal, in comparison with that of a standard sample, can be expressed numerically.

(c) *Volumetric Estimations*.—The best method is that of Löwenthal.<sup>2</sup> Five grams of whole cochineal are first boiled for one hour with 1½ litres of distilled water, the extract is poured through an ordinary tea-strainer, and the cochineal remaining in the strainer is again boiled for three-quarters of an hour with 1 litre of distilled water. After cooling and diluting to 2 litres, 100 c.c. of the resulting solution are diluted to 1 litre, treated with a measured volume of indigo-carmin solution and titrated with potassium permanganate. In the same way a good standard cochineal is treated and titrated. If, for example, the last plus the indigo solution require 25.6 c.c. of permanganate, the cochineal under examination plus the indigo solution require 21.0 c.c., and the indigo solution employed alone requires 11.2 c.c., then the amounts of dyestuff

<sup>1</sup> Muspratt's *Handbuch der technischen Chemie*, 3rd ed., vol. iii., p. 251.

<sup>2</sup> *Z. anal. Chem.*, 1877, 16, 179.

in the two cochineals are as 25.6—11.2:21.0—11.2, that is, as 14.2:9.8 or 100:68.05.

Penny<sup>1</sup> employs a standard solution of potassium ferricyanide for the estimation. One gram of finely powdered cochineal is boiled with 50 g. of dilute potassium hydroxide, and after the addition of 25 c.c. of water the mixture is treated drop by drop with a solution of 5 g. of potassium ferricyanide in 1 litre of water until the solution has a yellowish brown instead of a purple-red colour. The potassium ferricyanide is standardised by a solution of 1 g. of a standard cochineal in dilute potassium hydroxide.

Merson's<sup>2</sup> process depends on a volumetric determination of the quantity of sodium (or calcium) hypochlorite solution, containing 1 per cent. of active chlorine, required to decolorise a faintly ammoniacal extract of the finely powdered cochineal. About 20 c.c. of the hypochlorite solution would be required to decolorise 1 g. of the best cochineal. The colour value of such a sample is denoted by 100.

There is no direct relation between the percentage of ash and the colour value. The amount of ash in unadulterated cochineals, which is found to vary between 2.4 and 43.6 per cent. in the commercial products, ought not to exceed 4 per cent. according to Merson. Moreover it is only of secondary importance. Dark cochineal, as a rule, possesses a greater dyeing value than the silvery-grey, and also in general is less frequently adulterated. Barium sulphate, lime, and earthy substances are used as adulterants.

Garmin, like cochineal, can be estimated by the hypochlorite method. The amount of ash varies between 4.8 and 8.5 per cent., but is also of slight significance.

**Brazil Wood** occurs in many varieties (Brazil, St Martha, Nicaragua, Japan, Lima, Brasiliette, California, and Columbia wood) in Brazil, Central America, Jamaica, the Antilles, the East Indies, Japan, etc., and is brought on the market in the form of stout pieces, rasped, or as a powder, or finally as a liquid or a solid extract (for which the Lima and the St Martha woods in particular are employed). The dirty red-brown to blue-black wood is odourless, has a sweetish taste, and when chewed colours the saliva red. Ground Brazil wood differs from logwood by imparting a bright colour to cold water in about a quarter of an hour. The colours produced by Brazil wood are beautiful, but by no means permanent. Powdered Brazil wood no longer contains any dyestuff after 2 year's exposure to the light. On the other hand, a decoction of Brazil wood improves with time when kept cold and in the dark (due to fermentation, deoxidation of a few retarding substances,

<sup>1</sup> *J. prakt. Chem.*, 1857, 71, 119.

<sup>2</sup> *Pharm. J.*, 1900, 64, 309; cf. also J. M. Merrick's method of estimation by titration with permanganate, *Pharm. J.*, 1871 [ii.], 1, 906.

and separation of the tannin).<sup>1</sup> It is also a good plan to add a little skimmed milk during the extraction. Preliminary fermentation of the damp Brazil wood powder (moistened every few days with a solution of  $\frac{1}{2}$  kg. of gelatin in 100 kg. of water) has the effect of facilitating and improving the extraction of the dyestuff.

The substance forming the dyestuff of Brazil wood is brasilin, which is converted into brasilein by oxidation in alkaline solution in the air.

Brasilin is fixed on the fibre only in the form of a lake, usually the alumina lake. Almost its only uses are for shading other colours on cotton and for the preparation of wood brown on wool. The colours produced by Brazil wood are very unstable. The following estimations can be performed when estimating the value of Brazil wood or of its extracts:—

1. *Estimation of Water and Ash* with 5 g. of extract or 10 g. of chips.

2. *Colorimetric Examination* (especially of extracts).—Trimble's simple method<sup>1</sup> is used. The percentage of water in the extract having been previously determined, such a quantity of the extract is taken that 1 litre of the solution contains exactly 1 g. of dry extract. Also 2 g. of pure recrystallised copper sulphate are made up to a litre with water. Next, 1 c.c. of the extract solution (of the above concentration and prepared from the best commercial extract or from pure hæmatoxylin) is treated with 10 c.c. of water and 1 c.c. of the copper sulphate solution; the mixture is rapidly heated to boiling, poured into a graduated cylinder, and diluted to 100 c.c. with distilled water. The extract under examination is treated in exactly the same way, and its coloured solution is diluted with water in a similar graduated cylinder until both liquids, viewed from above, have exactly the same colour. On account of the rapidity with which its colour changes the type, solution must be renewed every ten to fifteen minutes.

3. *Dye-trials*.<sup>2</sup>—The decoction of 5 g. of extract or 20 g. of wood is diluted to 1 litre. If wool is employed for the dye-trial it is soaked in a solution containing 3 per cent. of potassium bichromate without the addition of any sulphuric acid, and is dyed in the extract solution, 10 c.c. for every 1 g. of wool. Before cotton is dyed it is placed in a solution of aluminium acetate (sp. gr. 1.037), wrung out, and suspended for some time in warm, damp air, or it is first treated with a solution of 3 per cent. of tannin, and then, without washing, with a solution of aluminium acetate or stannous chloride, or with a mixture of both (sp. gr. 1.037), and is then washed. For the dyeing, 20 c.c. of the extract solution are employed for every 1 g. of cotton.

"Purple lake red pale," "mean," and "dark" are light purple or

<sup>1</sup> *J. Soc. Dyers and Col.*, 1885, 1, 92.

<sup>2</sup> v. Cochenhausen, Muspratt's *Handbuch der technischen Chemie*, 3rd ed., vol. iii., p. 211.

darker purplish red lake dyes obtained by precipitating with sodium carbonate an aqueous extract of Brazil wood containing alum.<sup>1</sup> "Purple light red," a pale purple-red dye, is similarly prepared, a little magenta being added to the solution of the Brazil wood extract.

**Madder.**—Madder is the root of a perennial plant, *Rubia*, which is indigenous to Central Asia and Southern Europe. The commercial product, obtained by grinding the roots, is a yellowish, brown or brownish red powder; the entire roots (alizarin) are very rarely placed on the market.

The following adulterants have been found in it:—Brick dust, sand, clay, ochre, certain dye-woods (Brazil wood, sanders wood, etc.), substances containing tannin, etc.

The testing of madder as well as of madder preparations (Garancin) is performed by dye-trials.

**Safflower** consists of the dried petals of the *Carthamus tinctorius*, which flourishes especially in Egypt, in good quality; it contains a yellow dyestuff, insoluble in water, and a red dyestuff (carthamin), which is insoluble in water. To prepare the latter, a large quantity of safflower is extracted with cold water until the latter is only faintly coloured yellow. The mass is then strongly squeezed, macerated for some hours with a 0.15 per cent. solution of sodium carbonate, and again pressed; the liquid is filtered clear through canvas, the carthamin is precipitated by acetic acid and purified by repeated solution in alcohol and precipitation by water.<sup>2</sup> Carthamin occurs commercially in a solid form, under the name safflower red, and in a liquid form as safflower extract or safflower carmin. The quality of safflower is recognised by its fiery-red colour. Dull-coloured safflower has been gathered late or badly dried. Good safflower should not contain pieces of wood, leaves, sand, or blackened flowers. Carthamin, mixed with powdered chalk, is used as a red paint. In silk and cotton dyeing, safflower has been almost entirely superseded by artificial dyestuffs such as safranine, eosin, and rhodamine S. The fire of the colour is heightened by the addition of a little annatto. To produce very dark shades, one-third of archil is added.

**Dragon's blood** is obtained by boiling the red resinous juice of several kinds of calamus. The best kind occurs in dark brown balls, which produce a beautiful bright red powder by grinding. When heated, it evolves an odour of benzoic acid, of which it contains a small quantity. It dissolves very easily in alcohol and oils with a red colour, and in alkalis with a more violet colour. By reason of its deep, blood-red colour, it is frequently employed in making varnishes, etc.

**Cutch** (Catechu) is obtained by boiling the wood of the *Acacia*

<sup>1</sup> *Dingl. polyt. J.*, 1898, 308, 155.

<sup>2</sup> Cf. also Kametaka and A. G. Perkin, *Trans. Chem. Soc.*, 1910, 97, 1415.



*catechu*, the wood and the fruit of the *betel* or *arecanus*, with water, and evaporating the resulting solution to a syrupy consistence.

The chief kinds are: Bombay, Bengal, and Pegu cutch. They consist of large, irregular light to dark brown lumps, which dissolve in water with a dark brown colour and possess a bitter, astringent taste.

**Gambier** (*Yellow Catechu*, *Cubical Cutch*) is obtained by boiling the leaves of *Uncaria gambir*, and consists of opaque, brownish yellow dice, 3 to 4 cm. long, or blocks which are slightly soluble in cold water and dissolve almost completely in hot water.

Catechu and Gambier contain variable amounts of catechin, catechu-tannic acid and a brown substance, which is produced by the oxidation of the first during the manufacture. They possess a sweetish, astringent taste.

Gambier chiefly contains catechin. Greshoff<sup>1</sup> has described a method for its examination.

**Katechu** preparations are obtained by heating brown or yellow catechu with potassium bichromate or aluminium sulphate or copper sulphate.

Catechu and Gambier are employed in large quantities in cotton dyeing and printing, and in dyeing (weighting) silk.

The different kinds show distinct differences in colour, strength, and shade. Frequently it is found that mineral matter (sand, sodium chloride), starch, dextrin, and dried blood have been added.

Mineral constituents are determined by estimating the ash. Good kinds should not contain more than 3 to 4 per cent. of ash. The amount of water varies between 15 and 25 per cent.

Comparative dye-trials, or a search for adulterants, represent the only satisfactory method of testing the quality.<sup>2</sup>

**Kino** (Kino gum) is the thickened juice of *Pterocarpus marsupium*; it consists of small, glistening brown or blackish red pieces, and resembles catechu.

**Chestnut extract** is obtained from the wood of the horse-chestnut, and is put on the market in the form of glistening black pieces or as a brown syrup. It is used for producing black dyes, especially in silk dyeing. The examination is conducted similarly to that of catechu.

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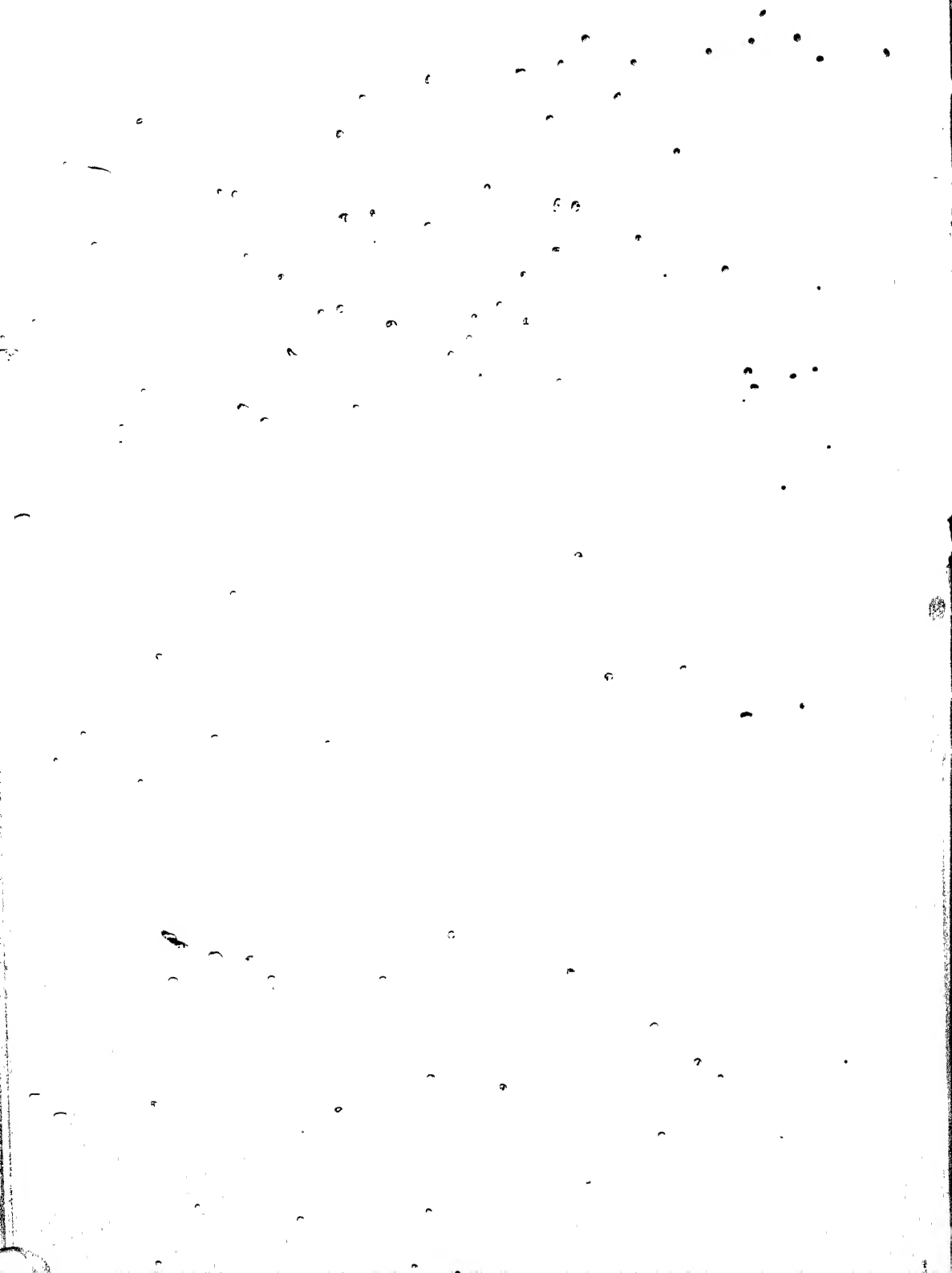
<sup>1</sup> *Pharm. Weekblad*, 1905, 42, 669; *J. Soc. Chem. Ind.*, 1905, 24, 1087.

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## ADDENDUM

Pages 1022-3, 1039-41, 1050 *et seq.* Compare also E. Grandmougin and M. Battegay, "Tabellarische Uebersicht der wichtigsten Küpenfarbstoffe nach dem Stande des Jahres 1910," *Elsässische Textil-Blatt*, 1911.



# APPENDIX

THIS APPENDIX COMPRISES THE TABLES INCLUDED  
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TABLE I. (*Text*, p. 103.)

Table of Charges for the Dry Assay of Silver Ores in Grams.

	Siliceous.	Basic.	Pyritic.	Cupriferous Pyritic.
Ore . . . . .	25	25	25	20
Red lead . . . . .	30	30	40	60
Charcoal . . . . .	1.5	2 to 3	...	...
Sodium carbonate . . . . .	40	20	30	20
Borax . . . . .	5	20	15	20

Table of Charges for the Dry Assay of Silver Ores  
in Assay Tons.

	Siliceous.	Basic.	Pyritic.	Cupriferous Pyritic.
Ore . . . . .	1.0	1.0	1.0	0.5
Red lead . . . . .	1.0	1.0	1.25	2.0
Charcoal . . . . .	0.05	0.06 to 0.1	...	...
Sodium carbonate . . . . .	1.0	0.75	1.0	0.5
Borax . . . . .	0.2	0.75	0.5	0.5

[*Note.*—Charges for ores containing stibnite, arsenical pyrites, cassiterite, tellurides, etc., are given under "Gold," pp. 127 *et seq.*]

TABLE II. (*Text*, p. 108.)Table for computing the Troy Weight of Gold or Silver  
per Long and Short Ton.

Per cent.	Per ton of 2240 lb.			Per ton of 2000 lb.			Per cent.	Per ton of 2240 lb.			Per ton of 2000 lb.		
	oz.	dwt.	gr.	oz.	dwt.	gr.		oz.	dwt.	gr.	oz.	dwt.	gr.
0.0001	...	...	16	...	...	14	0.06	19	12	0	17	10	0
0.0002	...	...	7	...	...	4	0.07	22	17	8	20	8	9
0.0003	...	...	1	...	...	18	0.08	26	2	16	23	6	17
0.0004	...	...	2	...	...	8	0.09	29	8	0	26	5	0
0.0005	...	...	3	...	...	22	0.1	32	13	8	29	3	8
0.0006	...	...	3	...	...	12	0.2	65	6	16	58	7	0
0.0007	...	...	4	...	...	2	0.3	98	0	0	87	10	0
0.0008	...	...	5	...	...	16	0.4	130	13	8	116	14	0
0.0009	...	...	5	...	...	6	0.5	163	6	16	145	17	0
0.001	...	...	6	...	...	20	0.6	196	0	0	175	0	0
0.002	...	...	13	...	...	16	0.7	228	13	8	204	4	0
0.003	...	...	19	...	...	12	0.8	261	6	16	233	7	0
0.004	...	...	1	...	...	8	0.9	294	0	0	262	10	0
0.005	...	...	1	...	...	4	1.0	326	13	8	291	14	0
0.006	...	...	1	...	...	0	2.0	653	6	16	583	8	0
0.007	...	...	2	...	...	20	3.0	980	0	0	875	2	0
0.008	...	...	2	...	...	16	4.0	1306	13	8	1166	16	0
0.009	...	...	2	...	...	12	5.0	1633	6	16	1458	10	0
0.01	...	...	3	...	...	8	6.0	1960	0	0	1750	4	0
0.02	...	...	6	...	...	16	7.0	2286	13	8	2041	18	0
0.03	...	...	9	...	...	0	8.0	2613	6	16	2333	12	0
0.04	...	...	13	...	...	8	9.0	2940	0	0	2625	6	0
0.05	...	...	16	...	...	16	10.0	3266	13	8	2916	14	0

TABLE III. (*Text*, pp. 360-73.)

## Tables of Specific Gravities of Metallic Salts.

*Ferrous Sulphate* at 15°. Gerlach.

Per cent. $\text{FeSO}_4 + 7\text{H}_2\text{O}$ .	Spec. grav.	Per cent. $\text{FeSO}_4 + 7\text{H}_2\text{O}$ .	Spec. grav.
1	1.005	15	1.082
2	1.011	20	1.112
3	1.016	25	1.143
4	1.021	30	1.174
5	1.027	35	1.206
10	1.054	40	1.239

*Ferric Sulphate* at 15°. Wolff.

Per cent. $\text{Fe}_2(\text{SO}_4)_3$ .	Spec. grav.	Per cent. $\text{Fe}_2(\text{SO}_4)_3$ .	Spec. grav.
5	1.0426	35	1.3782
10	1.0854	40	1.4506
15	1.1324	45	1.5298
20	1.1825	50	1.6148
25	1.2426	55	1.7050
30	1.3090	60	1.8006

*Ferric Chloride* at 17°.5. Franz.

Per cent. $\text{Fe}_2\text{Cl}_6$ .	Spec. grav.	Per cent. $\text{Fe}_2\text{Cl}_6$ .	Spec. grav.	Per cent. $\text{Fe}_2\text{Cl}_6$ .	Spec. grav.
2	1.015	22	1.175	42	1.387
4	1.029	24	1.195	44	1.412
6	1.044	26	1.216	46	1.437
8	1.058	28	1.237	48	1.462
10	1.073	30	1.257	50	1.487
12	1.086	32	1.278	52	1.515
14	1.105	34	1.299	54	1.544
16	1.122	36	1.320	56	1.573
18	1.138	38	1.341	58	1.602
20	1.154	40	1.362	60	1.632

## Tables of Specific Gravities of Metallic Salts—Continued.

*Potassium Chromate* at 19°.5. Kremers, Schiff, and Gerlach.

Per cent. $K_2CrO_4$ .	Spec. grav.	Per cent. $K_2CrO_4$ .	Spec. grav.	Per cent. $K_2CrO_4$ .	Spec. grav.	Per cent. $K_2CrO_4$ .	Spec. grav.
1	1.008	11	1.093	21	1.186	31	1.292
2	1.016	12	1.101	22	1.196	32	1.304
3	1.024	13	1.110	23	1.207	33	1.315
4	1.033	14	1.120	24	1.217	34	1.327
5	1.041	15	1.129	25	1.227	35	1.339
6	1.049	16	1.138	26	1.238	36	1.351
7	1.058	17	1.147	27	1.249	37	1.363
8	1.066	18	1.157	28	1.259	38	1.375
9	1.075	19	1.167	29	1.270	39	1.387
10	1.084	20	1.177	30	1.281	40	1.399

*Potassium Bichromate* at 19°.5. Kremers and Gerlach.

Per cent. $K_2Cr_2O_7$ .	Spec. grav.	Per cent. $K_2Cr_2O_7$ .	Spec. grav.	Per cent. $K_2Cr_2O_7$ .	Spec. grav.
1	1.007	6	1.043	11	1.080
2	1.015	7	1.050	12	1.087
3	1.022	8	1.058	13	1.095
4	1.030	9	1.065	14	1.102
5	1.037	10	1.073	15	1.110

*Sodium Bichromate.*

Per cent. $Na_2Cr_2O_7$ .	Spec. grav.	Per cent. $Na_2Cr_2O_7$ .	Spec. grav.
1	1.007	30	1.208
5	1.035	35	1.245
10	1.071	40	1.280
15	1.105	45	1.313
20	1.141	50	1.343
25	1.171		

*Zinc Sulphate* at 15°.

Per cent. $ZnSO_4+7H_2O$ .	Spec. grav.	Per cent. $ZnSO_4+7H_2O$ .	Spec. grav.
5	1.029	35	1.231
10	1.059	40	1.271
15	1.091	45	1.310
20	1.124	50	1.352
25	1.167	55	1.399
30	1.193	60	1.445

Tables of Specific Gravities of Metallic Salts—*Continued.**Zinc Chloride at 19°. Krämer.*

Per cent. $\text{ZnCl}_2$ .	Spec. grav.	Per cent. $\text{ZnCl}_2$ .	Spec. grav.
5	1.045	35	1.352
10	1.091	40	1.420
15	1.137	45	1.488
20	1.186	50	1.566
25	1.238	55	1.650
30	1.291	60	1.740

*Copper Sulphate at 15°.*

Per cent. $\text{CuSO}_4 + 5\text{H}_2\text{O}$ .	Spec. grav.	Per cent. $\text{CuSO}_4 + 5\text{H}_2\text{O}$ .	Spec. grav.	Per cent. $\text{CuSO}_4 + 5\text{H}_2\text{O}$ .	Spec. grav.
1	1.007	10	1.069	19	1.144
2	1.013	11	1.076	20	1.152
3	1.020	12	1.084	21	1.160
4	1.027	13	1.091	22	1.169
5	1.033	14	1.096	23	1.177
6	1.040	15	1.114	24	1.185
7	1.048	16	1.121	25	1.193
8	1.055	17	1.129		
9	1.062	18	1.137		

*Cupric Chloride at 17°. Franz.*

Per cent. $\text{CuCl}_2$ .	Spec. grav.	Per cent. $\text{CuCl}_2$ .	Spec. grav.	Per cent. $\text{CuCl}_2$ .	Spec. grav.
2	1.018	16	1.170	30	1.362
4	1.036	18	1.195	32	1.395
6	1.055	20	1.222	34	1.429
8	1.073	22	1.250	36	1.462
10	1.092	24	1.278	38	1.495
12	1.118	26	1.306	40	1.528
14	1.144	28	1.334		

*Stannous Chloride at 15°. Gerlach.*

Per cent. $\text{SnCl}_2 + 2\text{H}_2\text{O}$ .	Spec. Grav.	Per cent. $\text{SnCl}_2 + 2\text{H}_2\text{O}$ .	Spec. Grav.	Per cent. $\text{SnCl}_2 + 2\text{H}_2\text{O}$ .	Spec. Grav.	Per cent. $\text{SnCl}_2 + 2\text{H}_2\text{O}$ .	Spec. Grav.
2	1.013	22	1.161	42	1.352	62	1.613
4	1.026	24	1.177	44	1.374	64	1.644
6	1.040	26	1.194	46	1.397	66	1.677
8	1.054	28	1.212	48	1.421	68	1.711
10	1.068	30	1.230	50	1.445	70	1.745
12	1.083	32	1.249	52	1.471	72	1.783
14	1.097	34	1.268	54	1.497	74	1.821
16	1.113	36	1.288	56	1.525	75	1.840
18	1.128	38	1.309	58	1.554		
20	1.144	40	1.330	60	1.582		



## Tables of Specific Gravities of Metallic Salts—Continued.

*Stannic Chloride at 15°. Gerlach.*

Per cent. SnCl <sub>4</sub> .5H <sub>2</sub> O.	Spec. Grav.	Per cent. SnCl <sub>4</sub> .5H <sub>2</sub> O.	Spec. Grav.
5	1.030	45	1.320
10	1.059	50	1.366
15	1.091	55	1.416
20	1.124	60	1.468
25	1.158	65	1.526
30	1.195	70	1.587
35	1.235	80	1.727
40	1.276	90	1.893

TABLE IV. (*Text, pp. 364-68.*)

## Table of Solubilities of Metallic Salts.

One hundred parts of water dissolve:—

Parts.	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
K <sub>2</sub> CrO <sub>4</sub> . . .	58.90	60.92	62.94	64.96	66.98	69.0	71.02	73.04	75.06	77.08	79.10
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> . . .	4.6	7.4	12.4	18.4	25.9	35.0	45.0	56.7	68.6	81.1	94.1
ZnSO <sub>4</sub> . . .	43.02	48.36	53.13	58.40	63.52	68.75	74.20	79.25	84.60	89.78	95.03
ZnSO <sub>4</sub> +7H <sub>2</sub> O .	115.22	138.21	61.49	190.90	224.05	263.84	313.48	369.36	442.62	533.02	653.59
CuSO <sub>4</sub> +5H <sub>2</sub> O .	...	36.9	42.3	...	56.9	...	...	...	118.0	...	203.3
CuSO <sub>4</sub> . . .	...	20.9	23.5	...	30.3	...	...	...	53.1	...	75.3

TABLE V. (*Text, p. 594.*)

## Percentage of Calcium Carbide and corresponding Gas Yield of Acetylene.

F. B. Gatehouse.

Calcium Carbide.	Acetylene.	Acetylene.	Calcium Carbide.	Acetylene.	Acetylene.	Calcium Carbide.	Acetylene.	Acetylene.
Per cent.	Litres per kg.	Cub. feet per lb.	Per cent.	Litres per kg.	Cub. feet per lb.	Per cent.	Litres per kg.	Cub. feet per lb.
100	365.62	5.862	90	329.12	5.272	80	292.62	4.682
99	361.97	5.803	89	325.47	5.213	79	288.97	4.623
98	358.32	5.745	88	321.82	5.154	78	285.32	4.564
97	354.67	5.685	87	318.17	5.095	77	281.67	4.505
96	351.02	5.626	86	314.52	5.036	76	278.02	4.446
95	347.37	5.567	85	310.87	4.977	75	274.37	4.387
94	343.72	5.508	84	307.22	4.918	74	271.02	4.328
93	340.07	5.449	83	303.57	4.859	73	267.37	4.269
92	336.52	5.390	82	299.92	4.800	72	263.72	4.210
91	332.77	5.331	81	296.27	4.741	71	260.07	4.151
						70	256.42	4.092

TABLE VI. (*Text*, p. 593.)  
 Table for the Correction of the Volume of Acetylene in cubic feet to 60° F. and 30 in. pressure.  
 F. B. Gatehouse.

Milli- metres.	Inches.	°C. 10. °F. 50.	°C. 11-1. °F. 52.	°C. 12-2. °F. 54.	°C. 13-3. °F. 56.	°C. 14-4. °F. 58.	°C. 15-5. °F. 60.	°C. 16-6. °F. 62.	°C. 17-7. °F. 64.	°C. 18-8. °F. 66.	°C. 20. °F. 68.	°C. 21-1. °F. 70.	°C. 22-2. °F. 72.	°C. 23-3. °F. 74.	°C. 24-4. °F. 76.
721-36	28-4	970	965	960	955	951	946	941	936	931	926	921	915	910	905
723-90	28-5	973	968	964	959	954	949	944	939	934	929	924	919	914	908
726-44	28-6	977	972	967	962	958	953	947	943	938	932	927	922	917	912
728-98	28-7	980	975	970	966	961	956	951	946	941	936	931	925	920	915
731-52	28-8	984	979	974	969	964	959	954	949	944	939	934	929	924	918
734-06	28-9	987	982	977	973	968	963	958	953	948	942	937	932	927	921
736-60	29-0	990	986	981	976	971	966	961	956	951	946	941	935	930	925
739-14	29-1	994	989	984	979	975	969	964	959	954	949	944	939	933	928
741-68	29-2	997	992	988	982	978	973	968	962	958	952	947	942	937	931
744-22	29-3	1001	996	991	986	981	976	971	966	961	956	950	945	940	935
746-76	29-4	1004	999	995	990	985	980	975	969	964	959	954	949	943	938
749-31	29-5	1008	1003	998	993	988	983	978	973	968	962	957	952	947	941
751-85	29-6	1011	1006	1001	996	992	986	981	976	971	966	960	955	950	944
754-39	29-7	1015	1010	1005	1000	995	990	985	980	974	969	964	959	953	948
757-13	29-8	1018	1013	1008	1003	998	993	988	983	978	972	967	962	957	951
759-67	29-9	1022	1017	1012	1007	1002	997	991	986	981	976	970	965	960	954
762-21	30-0	1025	1020	1015	1010	1005	1000	995	990	985	979	974	968	963	958
764-75	30-1	1029	1024	1019	1014	1009	1003	998	993	988	983	977	972	966	961
767-29	30-2	1032	1027	1022	1017	1012	1007	1002	996	991	986	980	975	970	964
770-83	30-3	1036	1030	1025	1020	1015	1010	1005	1000	995	989	984	978	973	968
773-37	30-4	1039	1034	1029	1024	1019	1014	1008	1003	998	993	987	982	976	971
775-91	30-5	1042	1037	1032	1027	1022	1017	1012	1006	1001	996	991	985	980	975
778-45	30-6	1046	1041	1036	1031	1026	1021	1016	1011	1005	1000	995	989	984	978
780-99	30-7	1049	1044	1039	1034	1029	1024	1019	1014	1009	1003	998	993	987	982
783-53	30-8	1053	1048	1043	1037	1032	1028	1023	1018	1013	1007	1002	997	991	985
786-07	30-9	1056	1051	1046	1041	1036	1031	1026	1021	1016	1010	1005	1001	995	989

TABLE VII.

Table for the Correction of the Volume of Gas measured over Atmospheric Pressures to the Volume

BAR.	THERMOMETER—			FAHRENHEIT.		50°	52°	54°	56°	58°	60°
	40°	42°	44°	46°	48°						
28.0	.979	.974	.970	.965	.960	.956	.951	.946	.942	.937	.932
28.1	.983	.978	.973	.969	.964	.959	.955	.951	.945	.941	.936
28.2	.986	.981	.977	.972	.967	.962	.958	.953	.949	.944	.939
28.3	.990	.985	.980	.976	.971	.966	.961	.957	.952	.947	.942
28.4	.993	.988	.984	.979	.974	.970	.965	.960	.955	.951	.946
28.5	.997	.992	.987	.983	.978	.973	.968	.964	.959	.954	.949
28.6	1.001	.995	.991	.986	.981	.977	.972	.967	.962	.958	.953
28.7	1.004	.999	.994	.990	.985	.980	.975	.970	.966	.961	.956
28.8	1.007	1.003	.998	.993	.988	.984	.979	.974	.969	.964	.959
28.9	1.011	1.006	1.001	.997	.992	.987	.982	.977	.973	.968	.963
29.0	1.014	1.010	1.005	1.000	.995	.990	.986	.981	.976	.971	.966
29.1	1.018	1.013	1.008	1.004	.999	.994	.989	.984	.979	.975	.969
29.2	1.021	1.017	1.012	1.007	1.002	.997	.992	.988	.982	.978	.973
29.3	1.025	1.020	1.015	1.011	1.006	1.001	.996	.991	.986	.981	.976
29.4	1.028	1.024	1.019	1.014	1.009	1.004	.999	.995	.990	.985	.980
29.5	1.032	1.027	1.022	1.018	1.013	1.008	1.003	.998	.993	.988	.983
29.6	1.036	1.031	1.026	1.021	1.016	1.011	1.006	1.001	.996	.992	.986
29.7	1.039	1.034	1.029	1.025	1.019	1.015	1.010	1.005	1.000	.995	.990
29.8	1.043	1.038	1.033	1.028	1.023	1.018	1.013	1.008	1.003	.998	.993
29.9	1.046	1.041	1.036	1.031	1.026	1.022	1.017	1.012	1.007	1.002	.997
30.0	1.050	1.045	1.040	1.035	1.030	1.025	1.020	1.015	1.010	1.005	1.000
30.1	1.053	1.048	1.043	1.038	1.033	1.029	1.024	1.019	1.014	1.009	1.003
30.2	1.057	1.052	1.047	1.042	1.037	1.032	1.027	1.022	1.017	1.012	1.007
30.3	1.060	1.055	1.050	1.045	1.040	1.036	1.030	1.025	1.020	1.015	1.010
30.4	1.064	1.059	1.054	1.049	1.044	1.039	1.034	1.029	1.024	1.019	1.014
30.5	1.067	1.062	1.057	1.052	1.047	1.042	1.037	1.032	1.027	1.022	1.017
30.6	1.071	1.066	1.061	1.056	1.051	1.046	1.041	1.036	1.031	1.026	1.020
30.7	1.074	1.069	1.064	1.059	1.054	1.049	1.044	1.039	1.034	1.029	1.024
30.8	1.078	1.073	1.068	1.063	1.058	1.053	1.048	1.043	1.037	1.032	1.027
30.9	1.081	1.076	1.071	1.066	1.061	1.056	1.051	1.046	1.041	1.036	1.031
31.0	1.085	1.080	1.075	1.070	1.065	1.060	1.055	1.049	1.044	1.039	1.034

\* \* The numbers in the above table have been calculated from the formula  $n = \frac{17.64(h-a)}{460+t}$  scale, and  $a$  the tension of aqueous vapour at  $t^\circ$ . If  $v$  is any volume at  $t^\circ$ , and  $h$  inches

(Text, pp. 690-91.)

Water at different Temperatures and under different  
at 60° F. and 30 in. Bar. (moist).

62°	64°	66°	68°	70°	72°	74°	76°	78°	80°	82°	84°
·927	·922	·917	·912	·907	·902	·897	·892	·887	·881	·875	·870
·930	·926	·921	·916	·911	·905	·900	·895	·890	·884	·879	·873
·934	·929	·924	·919	·914	·909	·904	·898	·893	·887	·882	·876
·937	·932	·928	·922	·917	·912	·907	·902	·896	·891	·885	·880
·941	·936	·931	·926	·921	·915	·910	·905	·900	·894	·888	·883
·944	·939	·934	·929	·924	·919	·914	·908	·903	·897	·892	·886
·947	·943	·938	·932	·927	·922	·917	·912	·906	·901	·895	·889
·951	·946	·941	·936	·931	·925	·920	·915	·909	·904	·898	·893
·954	·949	·944	·939	·934	·929	·924	·918	·913	·907	·901	·896
·958	·953	·948	·942	·937	·932	·927	·921	·916	·910	·905	·899
·961	·956	·951	·946	·941	·935	·930	·925	·919	·914	·908	·903
·964	·959	·954	·949	·944	·939	·933	·928	·923	·917	·911	·906
·968	·963	·958	·952	·947	·942	·937	·931	·926	·920	·914	·909
·971	·966	·961	·956	·950	·945	·940	·935	·929	·923	·918	·912
·975	·969	·964	·959	·954	·949	·943	·938	·932	·927	·921	·915
·978	·973	·968	·962	·957	·952	·947	·941	·936	·930	·924	·919
·981	·976	·971	·966	·960	·955	·950	·944	·939	·933	·927	·922
·985	·980	·974	·969	·964	·959	·953	·948	·942	·937	·931	·925
·988	·983	·978	·972	·967	·962	·957	·951	·946	·940	·934	·928
·991	·986	·981	·976	·970	·965	·960	·954	·949	·943	·937	·932
·995	·990	·985	·979	·974	·968	·963	·958	·952	·946	·941	·935
·998	·993	·988	·983	·977	·972	·966	·961	·955	·950	·944	·938
1·002	·996	·991	·986	·980	·975	·970	·964	·959	·953	·947	·941
1·005	1·000	·995	·989	·984	·978	·973	·968	·962	·956	·950	·945
1·008	1·003	·998	·993	·987	·982	·976	·971	·965	·959	·954	·948
1·012	1·006	1·001	·996	·990	·985	·980	·974	·969	·963	·957	·951
1·015	1·010	1·005	·999	·994	·988	·983	·977	·972	·966	·960	·954
1·018	1·013	1·008	1·003	·997	·992	·986	·981	·975	·969	·963	·957
1·022	1·017	1·011	1·006	1·000	·995	·990	·984	·978	·972	·967	·961
1·025	1·020	1·015	1·009	1·004	·998	·993	·987	·982	·976	·970	·964
1·029	1·023	1·018	1·013	1·007	1·002	·996	·991	·985	·979	·973	·967

where  $h$  is the height of the barometer in inches,  $t$  the temperature on the Fahrenheit pressure, and  $V$  the corresponding volume at 60° and 30 inches pressure,  $V = v$ .

TABLE VIII. (*Text, p. 693.*)  
Table of the Caloric Power of Gases.

Gas.	Calories per cubic metre.						B. Th. U. per cubic foot.					
	0° C. and 760 mm. dry.		15° C. and 760 mm. dry.		15° C. and 760 mm. moist.		32° F. and 80 in. dry.		60° F. and 80 in. dry.		60° F. and 80 in. moist.	
	Gross.	Nett.	Gross.	Nett.	Gross.	Nett.	Gross.	Nett.	Gross.	Nett.	Gross.	Nett.
Hydrogen . . .	3056	2621	2897	2484	2848	2443	844	295	326	279	321	275
Carbon monoxide . . .	3056	...	2897	...	2848	...	844	...	326	...	321	...
Sulphuretted hydrogen . . .	6170	5745	5849	5446	5751	5355	693	645	657	612	646	602
Methane . . .	9572	8699	9074	8246	8922	8108	1076	977	1020	927	1003	911
Ethylene . . .	15068	14190	14279	13451	14041	13226	1692	1594	1605	1511	1578	1486
Propylene . . .	22186	20832	20983	19747	20633	19417	2487	2341	2358	2219	2319	2182
Benzene vapour . . .	35397	34093	33553	32318	32992	31777	3977	3831	3771	3631	3708	3570

*Further deduction from nett values to be made if the sensible heat of the condensed water evolved by the cooling from 100° to 15° C. is to be allowed for.*

	Calories per cubic metre.				B. Th. U. per cubic foot.			
	0° C. and 760 mm. dry.		15° C. and 760 mm. dry.		32° F. and 80 in. dry.		60° F. and 80 in. dry.	
For H <sub>2</sub> and H <sub>2</sub> S . . .	68	64.5	63	7.6	7.25	7.1		
" CH <sub>4</sub> and C <sub>2</sub> H <sub>4</sub> . . .	136	123	126	15.2	14.5	14.2		
" C <sub>3</sub> H <sub>6</sub> and C <sub>6</sub> H <sub>6</sub> . . .	204	193.5	189	22.8	21.75	21.3		

TABLE IX. (*Text*, p. 742.)  
 Specific Gravities of Solutions of Ammonia at 15°.  
 Lunga and Wiernek.

Sp. gr. at 15°.	Per cent. NH <sub>3</sub> .	1 litre contains NH <sub>3</sub> at 15° g.	Correction of the sp. gr. for ±1°.	Sp. gr. at 15°.	Per cent. NH <sub>3</sub> .	1 litre contains NH <sub>3</sub> at 15° g.	Correction of the sp. gr. for ±1°.
1.000	0.00	0.0	0.00018	0.940	15.63	146.9	0.00039
0.998	0.45	4.5	0.00018	0.938	16.22	152.1	0.00040
0.996	0.91	9.1	0.00019	0.936	16.82	157.4	0.00041
0.994	1.37	13.6	0.00019	0.934	17.42	162.7	0.00041
0.992	1.84	18.2	0.00020	0.932	18.03	168.1	0.00042
0.990	2.31	22.9	0.00020	0.930	18.64	173.4	0.00042
0.988	2.80	27.7	0.00021	0.928	19.25	178.6	0.00043
0.986	3.30	32.5	0.00021	0.926	19.87	184.2	0.00044
0.984	3.80	37.4	0.00022	0.924	20.49	189.3	0.00045
0.982	4.30	42.2	0.00022	0.922	21.12	194.7	0.00046
0.980	4.80	47.0	0.00023	0.920	21.75	200.1	0.00047
0.978	5.30	51.8	0.00023	0.918	22.39	205.6	0.00048
0.976	5.80	56.6	0.00024	0.916	23.03	210.9	0.00049
0.974	6.30	61.4	0.00024	0.914	23.68	216.3	0.00050
0.972	6.80	66.1	0.00025	0.912	24.33	221.9	0.00051
0.970	7.31	70.9	0.00025	0.910	24.99	227.4	0.00052
0.968	7.82	75.7	0.00026	0.908	25.65	232.9	0.00053
0.966	8.33	80.5	0.00026	0.906	26.31	238.3	0.00054
0.964	8.84	85.2	0.00027	0.904	26.98	243.9	0.00055
0.962	9.35	89.9	0.00028	0.902	27.65	249.4	0.00056
0.960	9.91	95.1	0.00029	0.900	28.33	255.0	0.00057
0.958	10.47	100.3	0.00030	0.898	29.01	260.5	0.00058
0.956	11.03	105.4	0.00031	0.896	29.69	266.0	0.00059
0.954	11.60	110.7	0.00032	0.894	30.37	271.5	0.00060
0.952	12.17	115.9	0.00033	0.892	31.05	277.0	0.00060
0.950	12.74	121.0	0.00034	0.890	31.75	282.6	0.00061
0.948	13.31	126.2	0.00035	0.888	32.50	288.6	0.00062
0.946	13.88	131.3	0.00036	0.886	33.25	294.6	0.00063
0.944	14.46	136.5	0.00037	0.884	34.10	301.4	0.00064
0.942	15.04	141.7	0.00038	0.882	34.95	308.3	0.00065

TABLE X. (*Text*, p. 747.)

Specific Gravities of Solutions of Ammonium Sulphate at 15°.

Per cent.	Sp. gr.	Per cent.	Sp. gr.	Per cent.	Sp. gr.	Per cent.	Sp. gr.
1	1.0057	14	1.0805	27	1.1554	40	1.2284
2	1.0115	15	1.0862	28	1.1612	41	1.2343
3	1.0172	16	1.0920	29	1.1670	42	1.2402
4	1.0230	17	1.0977	30	1.1724	43	1.2462
5	1.0287	18	1.1035	31	1.1780	44	1.2522
6	1.0345	19	1.1092	32	1.1836	45	1.2583
7	1.0403	20	1.1149	33	1.1892	46	1.2644
8	1.0460	21	1.1207	34	1.1948	47	1.2705
9	1.0518	22	1.1265	35	1.2004	48	1.2766
10	1.0575	23	1.1323	36	1.2060	49	1.2828
11	1.0632	24	1.1381	37	1.2116	50	1.2890
12	1.0690	25	1.1439	38	1.2172		
13	1.0747	26	1.1496	39	1.2228		

TABLE XI. (*Text*, p. 747.)

Specific Gravities of Solutions of Ammonium Chloride at 15°. Gerlach; Lunge and Köhler.

Per cent. NH <sub>4</sub> Cl.	Sp. gr.	Per cent. NH <sub>4</sub> Cl.	Sp. gr.	Per cent. NH <sub>4</sub> Cl.	Sp. gr.	Per cent. NH <sub>4</sub> Cl.	Sp. gr.
1	1.00316	8	1.02481	15	1.04524	22	1.06479
2	1.00632	9	1.02781	16	1.04804	23	1.06754
3	1.00948	10	1.03081	17	1.05086	24	1.07029
4	1.01264	11	1.03370	18	1.05367	25	1.07304
5	1.01580	12	1.03658	19	1.05648	26	1.07575
6	1.01880	13	1.03947	20	1.05929		
7	1.02180	14	1.04225	21	1.06204		

TABLE XII. (*Text*, p. 748.)

Specific Gravities of Solutions of Ammonium Carbonate at 15°. Lunge and Smith.

Degrees Twaddell.	Sp. gr. at 15°.	Per cent. of Ammonium Carbonate.	Alteration of sp. gr. for $\pm 1^\circ$ .	Degrees Twaddell.	Sp. gr. at 15°.	Per cent. of Ammonium Carbonate.	Alteration of sp. gr. for $\pm 1^\circ$ .
1	1.005	1.66	0.0002	15	1.075	22.25	0.0006
2	1.010	3.18	0.0002	16	1.080	23.78	0.0006
3	1.015	4.60	0.0003	17	1.085	25.31	0.0007
4	1.020	6.04	0.0003	18	1.090	26.82	0.0007
5	1.025	7.49	0.0003	19	1.095	28.33	0.0007
6	1.030	8.93	0.0004	20	1.100	29.93	0.0007
7	1.035	10.35	0.0004	21	1.105	31.77	0.0007
8	1.040	11.86	0.0004	22	1.110	33.45	0.0007
9	1.045	13.36	0.0005	23	1.115	35.08	0.0007
10	1.050	14.88	0.0005	24	1.120	36.88	0.0007
11	1.055	16.16	0.0005	25	1.125	38.71	0.0007
12	1.060	17.70	0.0005	26	1.130	40.34	0.0007
13	1.065	19.18	0.0005	27	1.135	42.20	0.0007
14	1.070	20.70	0.0005	28	1.140	44.29	0.0007

TABLE XII. (*Text*, pp. 768-69.)

Table for the Approximate Estimation of the Products obtained in the Distillation of Benzol. Davis.

A. Mixtures of 90 per cent. and 50 per cent. Benzol.

Benzol.		First Drop.	Percentage distilled at 100°.	Percentage distilled at 120°.
90 per cent.	50 per cent.			
0	100	92°	50	90
5	95	92°	51	92
10	90	91°	51.5	92
15	85	91°	53	92
20	80	90°	55	92
25	75	90°	60	93
30	70	90°	65	93
35	65	90°	67	94
40	60	88°	69	94
45	55	88°	70	94
50	50	87°	71	94
55	45	87°	73	94
60	40	86°	76	95
65	35	86°	78	95
70	30	86°	79	96
75	25	85°	84	96
80	20	85°	84	97
85	15	84°	86	97
90	10	84°	88	Dry
95	5	84°	89	"
100	0	84°	90	"

B. Mixtures of 50 per cent. Benzol and Commercial Toluene.

Mixture of		First Drop.	Percentage distilled at 100°.	Percentage distilled at 105°.	Percentage distilled at 110°.	Percentage distilled at 120°.
50 per cent. Benzol.	Toluene.					
00	0	92°	50	68	80	91
95	5	93°	45	64	76	91
90	10	94°	33	60	73	90
85	15	94°	30	58	73	90
80	20	95°	28	57	72	90
75	25	95°	26	55	71	90
70	30	96°	22	48	67	90
65	35	96°	19	47	65	90
60	40	96°	15	46	65	90
55	45	97°	12	44	65	90
50	50	98°	8	42	64	90
45	55	98°	4	34	57	90
40	60	99°	0	26	56	90
35	65	100°	0	25	55	90
30	70	100°	0	23	53	90
25	75	100°	0	21	53	90
20	80	100°	0	16	48	90
15	85	101°	0	14	46	90
10	90	102°	0	13	45	90
5	95	103°	0	10	44	90
0	100	103°	0	0	39	90



Table for the Approximate Estimation of the Products obtained in the Distillation of Benzol—*Continued*.

6. Mixtures of 90 per cent. Benzol and Commercial Toluene.

Mixture of		First Drop.	Percentage distilled at 100°.	Percentage distilled at 105°.	Percentage distilled at 110°.	Percentage distilled at 120°.
90 per cent. Benzol.	Toluene.					
0	100	103°	0	7	50	94
5	95	102°	0	21	59	94
10	90	101°	0	20	66	94
15	85	100°	0	38	68	95
20	80	97°	9	43	73	95
25	75	95°	16	53	76	95
30	70	95°	23	59	78	96
35	65	94°	33	60	80	96
40	60	93°	43	66	82	96
45	55	92°	46	71	85	97
50	50	91°	52	72	86	97
55	45	91°	58	76	86	97
60	40	91°	60	78	88	97
65	35	90°	65	81	89	97
70	30	89°	71	83	91	97
75	25	88°	75	85	91	98
80	20	87°	77	87	92	98
85	15	86°	83	89	93	98
90	10	85°	85	91	94	Dry
95	5	84°	88	93	95	"
100	0	84°	90	94	96	"

TABLE XIV. (*Text*, p. 806.)

Table of the Equivalent Weights of Anthraquinone and Anthracene. Lunge.

Anthraquinone.	Anthracene.	Anthraquinone.	Anthracene.	Anthraquinone.	Anthracene.
1	0.86	35	29.95	68	58.25
2	1.71	36	30.81	69	59.06
3	2.56	37	31.66	70	59.91
4	3.42	38	32.53	71	60.77
5	4.28	39	33.38	72	61.62
6	5.14	40	34.23	73	62.47
7	5.99	41	35.09	74	63.33
8	6.86	42	35.94	75	64.19
9	7.71	43	36.79	76	65.05
10	8.56	44	37.65	77	65.90
11	9.42	45	38.51	78	66.77
12	10.27	46	39.37	79	67.62
13	11.16	47	40.22	80	68.46
14	11.98	48	41.09	81	69.32
15	12.84	49	41.94	82	70.17
16	13.70	50	42.79	83	71.02
17	14.55	51	43.65	84	71.88
18	15.42	52	44.50	85	72.74
19	16.27	53	45.35	86	73.60
20	17.12	54	46.21	87	74.45
21	17.98	55	47.07	88	75.32
22	18.83	56	47.93	89	76.17
23	19.68	57	48.78	90	77.02
24	20.54	58	49.65	91	77.88
25	21.40	59	50.50	92	78.73
26	22.26	60	51.35	93	79.58
27	23.11	61	52.21	94	80.44
28	23.98	62	53.06	95	81.30
29	24.83	63	53.91	96	82.16
30	25.67	64	54.77	97	83.01
31	26.53	65	55.63	98	83.87
32	27.38	66	56.49	99	84.73
33	28.23	67	57.34	100	85.58
34	29.09				

TABLE XV. (*Text*, p. 364.)Table of the Specific Gravities of Mixtures of *o*- and *p*-Toluidine.

Lunge.

(a) at 15°, referred to water at 15°.

Spec. Grav.	Per cent. <i>o</i> -Toluidine.	Spec. Grav.	Per cent. <i>o</i> -Toluidine.	Spec. Grav.	Per cent. <i>o</i> -Toluidine.
1.0037	100	1.0015	82	0.9993	64
1.0036	99	1.0014	81	0.9992	63
1.0035	98	1.0013	80	0.9991	62
1.0034	97	1.0012	79½	0.9990	61½
1.0033	96	1.0011	78½	0.9989	61
1.0032	95	1.0010	77½	0.9988	60
1.0031	94	1.0009	77	0.9987	59
1.0030	93½	1.0008	76	0.9986	58½
1.0029	92½	1.0007	75	0.9985	58
1.0028	91½	1.0006	74	0.9984	57½
1.0027	91	1.0005	73	0.9983	56½
1.0026	90	1.0004	72½	0.9982	56
1.0025	89½	1.0003	72	0.9981	55
1.0024	88½	1.0002	71	0.9980	54½
1.0023	88	1.0001	70	0.9979	54
1.0022	87	1.0000	69	0.9978	53
1.0021	86½	0.9999	68½	0.9977	52½
1.0020	86	0.9998	68	0.9976	51½
1.0019	85	0.9997	67	0.9975	51
1.0018	84½	0.9996	66½	0.9974	50
1.0017	83½	0.9995	65½		
1.0016	82½	0.9994	65		
(b) at 20°, referred to water at 15°.					
0.9939	50	0.9934	46½	0.9929	43
0.9938	49½	0.9933	46	0.9928	42
0.9937	48½	0.9932	45	0.9927	41
0.9936	48	0.9931	44½	0.9926	40
0.9935	47½	0.9930	44		

TABLE XVI. (*Text*, p. 894.)

## Specific Gravities of Solutions of Methyl Alcohol.

Doroszewski and Roshdestwenski.

Methyl alcohol.	Spec. Grav. at 15°/15°.	Methyl alcohol.	Spec. Grav. at 15°/15°.	Methyl alcohol.	Spec. Grav. at 15°/15°.
per cent.		per cent.		per cent.	
0	1.00000	34	0.94817	68	0.88048
1	0.99814	35	0.94653	69	0.87816
2	0.99630	36	0.94487	70	0.87584
3	0.99457	37	0.94319	71	0.87347
4	0.99285	38	0.94149	72	0.87109
5	0.99116	39	0.93976	73	0.86868
6	0.98950	40	0.93802	74	0.86622
7	0.98787	41	0.93625	75	0.86376
8	0.98633	42	0.93447	76	0.86126
9	0.98480	43	0.93266	77	0.85876
10	0.98327	44	0.93082	78	0.85626
11	0.98179	45	0.92896	79	0.85374
12	0.98031	46	0.92708	80	0.85122
13	0.97887	47	0.92517	81	0.84868
14	0.97745	48	0.92323	82	0.84610
15	0.97603	49	0.92128	83	0.84348
16	0.97462	50	0.91932	84	0.84082
17	0.97322	51	0.91738	85	0.83815
18	0.97181	52	0.91531	86	0.83548
19	0.97040	53	0.91328	87	0.83280
20	0.96899	54	0.91124	88	0.83010
21	0.96758	55	0.90918	89	0.82740
22	0.96617	56	0.90710	90	0.82468
23	0.96476	57	0.90500	91	0.82196
24	0.96335	58	0.90289	92	0.81921
25	0.96192	59	0.90075	93	0.81639
26	0.96047	60	0.89859	94	0.81356
27	0.95901	61	0.89641	95	0.81070
28	0.95752	62	0.89419	96	0.80784
29	0.95601	63	0.89195	97	0.80498
30	0.95449	64	0.88968	98	0.80213
31	0.95296	65	0.88739	99	0.79929
32	0.95139	66	0.88510	100	0.79647
33	0.94979	67	0.88280		

TABLE XYII. (*Text*, p. 896.)

Temperature of Solidification of Solutions of Acetic Acid.

Rüdorff.

100 parts of Acetic Acid are mixed with	100 parts of the mixture contain	Temperature of Solidification.
0.0 Water	0.0 Water	+16°.7
0.5 "	0.497 "	+15°.65
1.0 "	0.980 "	+14°.8
1.5 "	1.477 "	+14°.0
2.0 "	1.961 "	+13°.25
3.0 "	2.912 "	+11°.95
4.0 "	3.846 "	+10°.5
5.0 "	4.761 "	+ 9°.4
6.0 "	5.660 "	+ 8°.2
7.0 "	6.542 "	+ 7°.1
8.0 "	7.407 "	+ 6°.25
9.0 "	8.257 "	+ 5°.3
10.0 "	9.090 "	+ 4°.3
11.0 "	9.910 "	+ 3°.6
12.0 "	10.774 "	+ 2°.7
15.0 "	13.043 "	- 0°.2
18.0 "	15.324 "	- 2°.6
21.0 "	17.355 "	- 5°.1
24.0 "	19.354 "	- 7°.4

# INDEX

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